

SOME REACTIONS OF ALUMINUM IN ACID
SOILS AND THEIR IMPLICATIONS
CONCERNING ROOT GROWTH

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Dept. of Agronomy & Soil Sci
Univ. of Hawaii
Project 138
march, 1960

~~J. C. Moorman~~

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AND THEIR IMPLICATIONS CONCERNING
ROOT GROWTH

by
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A thesis submitted to the Graduate Faculty
of North Carolina State College
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

Department of Soils

Raleigh

1959

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BIOGRAPHY

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ACKNOWLEDGMENTS

The author wishes to express appreciation to the graduate committee; Dr. N. T. Coleman, Dr. R. J. McCracken, Dr. S. B. Weed, Dr. J. F. Lutz, Dr. H. T. Scofield and Dr. Heinz Seltmann for their advice and assistance.

Special acknowledgment is made to Dr. N. T. Coleman for his stimulating interest and helpful advice throughout the course of this study. Appreciation is expressed to Miss Doris Craig for technical assistance. Appreciation is expressed to the author's wife, Irene, for assistance during the course of this study and in the preparation of this manuscript.

The author is indebted to the National Science Foundation for fellowship support.

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INTRODUCTION

It has long been recognized that the extremes of soil acidity are detrimental to the growth of many plants. Although much research has been aimed at finding causes for injury and at establishing bases for ameliorating treatments, many facets of the problem remain to be investigated.

Much of the early work concerning plant growth on acid soils indicated that "active aluminum" is quite toxic. A common observation was that concentrations of aluminum ions sufficient to cause injury to most plant species occurred in water extracts of acid soils. Salt solution extracts of such soils contained even larger quantities of aluminum. The pioneering work, however, did not provide adequate explanations for the source, the chemical form, or the reactions in soils of the "active aluminum". Perhaps because of these limitations, there was not a general acceptance that aluminum toxicity was a primary cause for restricted plant growth on acid soils.

More recent work on ion exchange in acid soils has shown the general prevalence of aluminum ions on the exchange sites of clay minerals. Aluminum ions, though strongly adsorbed, participate in exchange equilibria. It is then reasonable to suppose that aluminum concentrations in soil solutions are governed, at least in part, by such exchange equilibria, and that a more general understanding of aluminum toxicity can be

obtained from the coordinated study of plant behavior and ion exchange.

Because many soils in the southeastern United States, particularly in subsoil horizons, have a large part of their exchange capacity aluminum saturated, it was decided to measure exchangeable aluminum, soil solution aluminum and soil reaction, and to relate these to one another and to root growth in soils. Root growth rather than top growth was studied, because roots are more sensitive to acid soil injury. Also, good root growth is a prerequisite of good top growth, especially in years when water is limiting.

The project which furnished the data for this thesis was set up to study the following:

1. The extent to which aluminum restricts the growth of roots into a variety of North Carolina subsoils.
2. The effects of fertilizer and lime applications on soil solution concentrations of aluminum and on root growth.
3. The characterization of soils with regard to their contents of "available aluminum".

LITERATURE REVIEW

Aluminum ions have a high charge ($3+$) and are relatively small (ionic radius of 0.57 A). The high charge and small size account for the tenacity with which Al is held to exchange spots, and the strong bonds it forms with oxygen and other anions. Goldschmidt (1937) points out that elements with a low ratio of charge to radius tend to form more or less soluble cations; elements having a high ratio of charge to radius form anions with oxygen. Aluminum, Be, Ti, Th, Zr, and Hf are intermediate between these two groups and tend to form oxides insoluble in neutral solutions. In unbuffered solutions such cations hydrolyze to a greater or lesser extent, depending on the pH of the medium.

Although this project was aimed to investigate the factors limiting root growth in acid subsoils, the literature review is confined primarily to the effects of Al on plant growth and its reactions in soils. This procedure was followed for three reasons: 1) Only chemical factors affecting root growth were studied; 2) Although Fe and Mn are recognized as possible toxic substances in acid soils, for the soils studied the quantities of these ions in the exchangeable form were small as compared with that of Al; 3) Even though Ca deficiencies, as the cause of acid soil injury to plants, have been considered extensively in the past, the idea of toxic substances limiting growth seems more tenable.

Observed Aluminum Toxicities to Various Plants

The possible existence of toxic quantities of Al in forms available to plants has been considered for a number of years. Some of the evidence bearing on this is summarized below. Since much of the work examined was aimed both at establishing causes for poor plant growth on acid soils and at finding ameliorating treatments, the two matters are considered together.

The idea that soluble Al exists in acid soils, and that it may have a detrimental effect on plant growth, apparently was originated by Abbott, et al. (1913). They found a definite inverse relation between the growth of corn and the degree of soil acidity. This they attributed to the comparatively large amounts of soluble Fe and Al found in acid soils. Miyake (1916) found that concentrations of Al in solution cultures greater than $4.4 \times 10^{-4}M$ were toxic to rice seedlings. Hartwell and Pember (1918) attributed the poor growth of barley on acid soil, as compared with rye, to the greater tolerance of rye to soil-solution Al. In addition, they found that both lime and phosphate were effective in reducing the "active Al" in acid soils and thus increasing plant growth. Mirasol (1920) investigated the reasons for the failure of sweet clover on a strongly acid soil, and concluded that "soluble Al salts" in the soil were responsible. Treating the soil with lime greatly increased plant growth, phosphate

was beneficial, but the combination of the two gave the best plant growth.

Conner and Sears (1922) investigated the relative effects of Al-ions and H-ions on the growth of rye, barley and popcorn. They used various nutrient solutions, and found different relative effects of the H-ions and Al-ions in different solutions. In Shives nutrient solution, where Al toxicities were least, a precipitate was noted. This was very likely $\text{Al}(\text{OH})_3$ or aluminum phosphate, in which case Al toxicity could not occur. They concluded, as had Hartwell and Pember (1918) and Miyake (1916), that Al-ions were more toxic to barley than H-ions, and that toxicity was reduced when large quantities of phosphate were employed. The growth of rye was only slightly reduced by the concentrations of Al employed, and the corn seemed insensitive. Mather (1922) observed that timothy and red clover made very poor growth on an unlimed Miami silt loam, but redtop and alsike clover grew well. He attributed these results to differences in the sensitivity of the plants to Al toxicity.

Blair and Prince (1923), Mirasol (1920) and Howard (1919) made extensive studies of the poor growth of plants on soils given continuous treatments of ammonium sulfate. The extremely acid soils which resulted from continued use of $(\text{NH}_4)_2\text{SO}_4$ were attributed to the acid produced in the nitrification process. Blair and Prince (1923) water-leached 5 kgm of soil from limed and unlimed Sassafras soil, which had received

$(\text{NH}_4)_2\text{SO}_4$ continually for fifteen years. Analysis of the first liter of leachate from the unlimed soil showed 15 ppm Al and 3 ppm Fe. The amounts of the ions in the leachate from the limed soil were below the limits of detection. The pH of the extract from the unlimed soil was 4.7 and from the limed soil 6.8. The unlimed soil leachate was given numerous treatments, and barley plants were grown in it. By far the most effective treatment for increasing plant growth was the addition of NH_4OH , boiling and filtering. The addition of limestone or basic slag to the soil was the most effective treatment in increasing the soil pH and growth of barley. Also very effective was roasting the acid soil; a treatment which increased plant growth from 0 to 4.1 g per pot and the soil pH from 4.1 to 5.6.

Miyake, et al. (1924) studied the effect of cations and anions on the growth of barley by treating four acid mineral soils of Japan with the Ca, K and Na salts of CO_3 , HPO_4 , H_2PO_4 , SiO_3 and SO_4 . The HPO_4 and H_2PO_4 salts increased the total weight of plants about thirty-fold, the CO_3 salts about six-fold, and the SiO_3 salts about four-fold, while the SO_4 salts depressed growth. There was little difference between cations. The ability of the salts to precipitate Al from pure solutions of AlCl_3 was in the order $\text{CO}_3 > \text{HPO}_4 > \text{H}_2\text{PO}_4 > \text{SiO}_3$. No Al was precipitated from solution by SO_4 . Measurements showed that SO_4 increased the amounts of soluble Al in the soils.

Magistad (1925) made extensive studies of the Al contents of soil solutions and their relation to pH and to plant growth. Using a variety of soils and adding acid or base to get a wide pH range, he found the quantities of Al in soil solutions to be extremely low if the pH of the soil was between 4.7 and 8.5, but to increase rapidly below or above this range. In solution culture studies, noticeable Al injury to tops and roots occurred when pH values of the expressed tissue were less than those indicated below:

	<u>Roots</u>	<u>Tops</u>
Barley	5.0	6.0
Rye	4.2	5.0
Alfalfa	5.0	5.0
Corn	4.7	5.6
Oats	5.6	5.6
Soybeans	5.6	6.0
Red Clover	4.7	5.6

McLean and Gilbert (1927) found wide variations in the sensitivity of different plants to Al. They grew the plants by alternating them between solution cultures containing PO_4 or Al. Some precautions were taken to prevent the pH of the solutions from going so high that Al was precipitated from solution. Of the crops tested, lettuce, beets, timothy, and barley were the most sensitive. The growth of these was depressed by 2 ppm Al. Radishes, sorghum, cabbage, oats and rye, which were moderately sensitive, were injured by 7 ppm Al.

Corn, turnips and red top were found to be resistant to Al toxicity, their growth being depressed by 14 ppm Al. The first symptoms of Al injury were dwarfing and discoloration of roots, later the entire plant was injured.

Pierre (1931) investigated acid soil injury to corn, sorghum and barley grown on a number of southeastern soils. Most of these soils, before treatment, had pH's between 5.0 and 6.0. The conclusion was drawn that Al toxicities occurred, but that base saturation was more important. Their data, however, show a marked decrease in plant growth, particularly for barley, where the soil pH was below 5.0.

Ligon and Pierre (1932) made careful solution culture studies of the minimum concentrations of Al toxic to corn, sorghum, and barley. Precautions were taken to maintain constant pH and ion concentrations. They attributed the variable results of earlier workers to poor control of these factors. Results of the study showed that 1 ppm of Al was injurious to all three plants. The order of injury was, barley > sorghum > corn. There was a small reduction of plant growth in solutions brought to pH 4.5 with acid versus those at pH 6.0, but the depression was small in comparison to that caused by 1 ppm Al solution, pH 4.5.

Watenpaugh (1936) characterized the growth of alfalfa roots in the surface and subsoil of a Dekalb silt loam. A pH of 4.8 checked root penetration almost entirely, but roots grew well when the pH was 5.0. Pohlman (1946) found that the

addition of lime to an acid Gilipin silt loam caused a 50 per cent increase in the growth of alfalfa roots. Longnecker and Merkle (1952) studied the effect of lime placement in a soil on the root growth of crimson clover. Extensive root growth occurred only in soil horizons which had been limed. This brought them to the conclusion that the neutralizing effect of lime extends over a small area surrounding the dissolving lime particle, and that lime should be thoroughly mixed into the entire soil zone in which roots are expected to develop. The chief benefit of liming was attributed to its decreasing the solubility of Al and Mn, and possibly increasing the availability of phosphorus. Younts and York (1956) found no significant increase in root growth or top yields due to subsoil liming of a virgin Norfolk sandy loam, pH 5.5. They concluded that the soil was not sufficiently acid to seriously limit root growth.

Heslep (1951) studied the reasons for the poor growth of Romaine lettuce on two California surface soils, pH 4.9 and 4.8. The conclusions were drawn that neither Mn or Al toxicity, nor Ca deficiency, was responsible for the poor growth which was observed. The conclusion that no Al injury occurred came partly from the fact that a 1:2 soil-water extract of the soil had a maximum Al concentration of 0.39 ppm, a concentration deemed too small to cause injury. Vlamis (1953), however, conclusively showed that Al toxicity was the primary factor responsible for poor plant growth on an acid California soil.

He displaced the soil solution from an unlimed soil and a limed sub-sample, and grew barley plants in the resulting solutions. The plants grown on the pH 4.2 solution (1.8 ppm Al) displaced from the unlimed soil grew as well as those on the pH 5.8 solution displaced from the limed soil, only when $\text{Ca}(\text{OH})_2$ or NaOH were added. The addition of H_2SO_4 to the solution from the limed soil, in amounts sufficient to lower the pH to that of the solution from the unlimed soil, did not seriously reduce shoot and root growth, nor did the addition of both H_2SO_4 and MnSO_4 . When $\text{Al}_2(\text{SO}_4)_3$ was added, in the amount equal to the Al concentration in the soil solution from the unlimed soil, shoot and root growths were reduced to 70 and 30 per cent of maximum, respectively.

Not all plants are injured by Al. Ferns, blueberries, citrus and tea plants, which are Al accumulators, grow well on quite acid soils. Chenery (1955) found the Al content of tea plants to range from 100 ppm in stems to about 20,000 ppm in the old leaves of the plant. He attributed the failure of tea plants to grow on soils with pH's greater than 6.0 to the absence of available Al, rather than to an excess of Ca. These soils had little or no Al which could be removed by leaching with 1N NaCl. Chenery concluded that the tea bush, like other Al accumulators, may be a relic plant which owes its survival to cultivation.

Liebig, et al. (1942) found that the growth of orange and lemon cuttings was stimulated by 0.1 ppm Al in culture solutions

which had been purified to remove minor elements. They concluded, however, that this in no way proved the essentiality of Al. Somewhat higher Al concentrations were found to be toxic.

Albrecht and co-workers (1943) have made extensive studies to show that acid soil injury of plants was largely due to a Ca deficiency. Mehlich and Coleman (1952) pointed out the importance of percentage base saturation on growth of plants, but Coleman, Kamprath and Weed (1958) recognized the possibility of Al toxicity and questioned the significance of some of the earlier work.

It is well established that Al is toxic to plants, though the matter of critical concentrations for various plant species is only partially understood and depends, no doubt, on a number of environmental factors as well as on species. Again, the exact soil pH below which Al toxicity will occur is not known, but it seems to be around 5.0.

Possible Mechanisms of Aluminum Toxicity

Of the entire subject of Al toxicity, perhaps the least understood phase is the mechanism of plant injury. The proposed mechanisms fall loosely into three categories; 1) aluminum-induced phosphate deficiency, 2) antagonistic effects of Al on the absorption of Ca and other cations, and 3) effects of Al on various plant constituents.

Aluminum-induced phosphate deficiency. Hemwall (1957) and Thorup (1957) discussed the effects of exchangeable and

hydrous oxides of Al on reducing the concentrations of phosphorus in soil solutions. Others have suggested that there are other aluminum phosphate reactions which are significant in plant nutrition.

Burgess and Pember (1923) (as cited by Pierre and Stuart, 1933) found that the phosphate content of plant tops was much higher when grown on limed soil than on acid soil. They concluded that the beneficial effect of large applications of phosphate in correcting Al toxicity takes place within the plant, rather than in the soil. Pierre and Stuart (1933) found reduced concentrations of phosphate in the plant sap of lettuce plants suffering Al toxicity, and stated that large applications of phosphate to acid soils not only reduced Al toxicity by precipitating Al from the soil solution, but also by precipitating it within the plant.

Wright (1937) noted that the gross appearance of roots grown in phosphate-deficient and Al-toxic solution cultures was very similar. The roots were severely stunted, brittle, and reddish-purple in color. He concluded that Al caused a phosphorus deficiency by precipitating phosphate in the plant roots. Additional solution culture studies by Wright (1943) were interpreted to support his original hypothesis. He found that all of the phosphate in the tops and roots of barley plants grown in normal culture solutions was extracted by pH 3 H_2SO_4 , but that a pH 1 solution was required to

extract all of the phosphate from the roots of plants grown in solutions containing 8 ppm Al. More than twice as much phosphate was accumulated by the roots which had grown in the solution cultures containing 8 ppm Al. Additional work by Wright (1945, 1953) supports the conclusions of his earlier studies.

Ragland and Coleman¹ found that the roots of intact grain sorghum seedlings grown in phosphate solutions containing 2.25 ppm Al, accumulated about five times as much phosphate as those grown in the absence of Al. Aluminum had a similar effect on phosphate uptake by excised snap bean roots.

Wallihan (1948) was quite critical of the conclusion reached by Burgess and Pember (1923), Pierre and Stuart (1933) and Wright (1937, 1943, 1945, 1953), that Al is precipitated as aluminum phosphate in plant roots. He proposed instead that Al is accumulated in roots by its attraction to exchange sites, and the phosphate is, in turn, attracted and held by the Al. Quellette and Dessureaux (1958) studied the variable tolerance of different clones of alfalfa to Al and Mn toxicities. They concluded that the degree of tolerance was not due to Al-induced phosphate deficiency. Foster and Russell (1958), studying the effect of ferric iron on the uptake of phosphate by barley and rye, concluded that phosphate is accumulated in roots by attraction to Fe ions, which have combined with

¹J. L. Ragland and N. T. Coleman. Unpublished data. Soils Department, North Carolina State College.

immobile organic molecules. The atomic ratio of iron to phosphate appeared to be one. They stated, however, that Al does not function in this way.

Aleshin and Iostrellov (1949) placed wheat seedlings in phosphate buffers ranging from pH 4.1 to 8.0 and measured the root potential of the seedlings twenty-four hours later. At pH 4.1 the potential was positive; at higher pH values it became progressively lower; and, at pH 6.3 it was negative. When the roots were transferred to 0.001M $AlCl_3$ for ten minutes, their charge was reversed and they became positive.

There is good evidence that Al which accumulates in or on roots increases the amount of phosphate accumulated. Whether precipitation in the roots as $AlPO_4$, adsorption on exchange sites, or some other kind of reaction occurs is not known. It does seem certain, however, that most of the Al which becomes associated with plant roots stays there. The literature is replete with observations that very little Al is translocated to the tops of most plants, regardless of the intensity of Al injury.

Effect of Al on concentration of other cations in the plant. Because this study was concerned with the effects of soil acidity on root growth, Ca was an ion of particular interest. Among other things, Ca is important to root activity because of the "Viets effect" (Viets, 1944) and because of its stimulation of root cell elongation (Burstrom, 1954). Florell (1956) found that Ca in the substrate caused

a 54 per cent increase in root mitochondria, and also that the percentage protein in the mitochondria was larger when Ca was supplied. Any inhibition of these or other Ca-effects by Al would have important consequences. There are some indications that Al may interfere with the uptake of Ca by roots, though the matter is not clear.

Fried and Peech (1946) found that plants grown on limed soils absorbed much more Ca and gave higher yields than those grown on gypsum-treated soils, despite the higher Ca concentrations in the soil solutions where CaSO_4 had been added. It was concluded that Mn, and perhaps Al and Fe, which were brought into solution through exchange with Ca from the gypsum, prevented the uptake of Ca. Schmehl, et al. (1952) found that Al and, to a lesser extent, Mn and H reduced the rate of Ca uptake by alfalfa. Work by Mathers (1956) showed that barley and rye plants grown on acid soils had much smaller Ca and Mg contents than did plants grown on the same soils to which lime had been added. Sand culture studies by Harward, et al. (1955) showed that Al and Fe in the substrate, but not Mn, decreased the Ca content of old lettuce leaves. New leaves were not affected. Jackson (1957) noted that 5 meq. of Al per liter of nutrient solution not only prevented absorption of Ca by excised roots of snap beans, but caused a loss of Ca from the roots to the solution. Quellette and Dessureaux (1958) attributed the lower sensitivity of some alfalfa clones to Al and Mn toxicities to their ability to absorb more Ca and keep more of it in an "active" form. The

criterion used for "active" Ca was its solubility in water. Calcium was found to decrease the uptake of Mn and Al by the alfalfa roots, and was considered to immobilize part of the absorbed Mn and Al within the roots.

Mathers (1956) noted that corn plants grown in solution cultures containing 10 ppm Al showed iron deficiency symptoms. Harward, et al. (1955) found that Al in nutrient solutions decreased the K and Cu contents of new leaves of lettuce plants grown in the nutrient solution. The Mg, K and Cu content of old leaves also was decreased by Al.

From the above, it appears that Al in the substrate may have inhibitory effects on the absorption and translocation of other ions. The mechanism, and indeed the qualitative features of this, have not been established.

Effect of Al on specific plant constituents. The fact that the most sensitive stage, in the growth of plants, to Al toxicities is the seedling stage, suggests some type of injury other than disruption of the normal ion uptake processes. The plant is least dependent upon ion absorption in the seedling stage. Aluminum ions in plant cells may influence metabolic processes by interacting with enzymes, substrates or co-factors. Though Rarison (1958) concluded that Al toxicity is non-metabolic, and does not depend upon active uptake of Al, there have been a number of observations which indicate biochemical effects of Al.

Fluri (1908) (as cited by Magistad, 1925) showed that Al, added to nutrient solution, decreased the rate of starch

formation in plants. From this, he concluded that Al reduced diastase activity. Szucs (1921) (as cited by Magistad, 1925) concluded that Al was toxic to plants because it coagulates the protoplasm. It was his opinion that the stunted, thickened roots of plants grown in solutions containing Al salts were impervious to other ions. Stoklasa, et al. (1922) (as cited by Magistad, 1925) found that when Al was taken up by certain plants it coagulated the protein, a condition which he felt would allow other cations such as Ca and K to migrate out of cells. Smith (1928) discussed the well-known pickling effect of Al-ions, from alum, on cucumbers and cherries. It is doubtful that such considerations are pertinent, except perhaps at quite high Al concentrations. McLean and Gilbert (1927) found that Al absorbed by corn plants accumulated in the root cortex, mainly in the protoplasm, and that it was concentrated in the nuclei of the cells. No Al accumulation was detected in any part of the young corn plant except in the cortex of the immersed roots.

Leger, et al. (1958) have thoroughly characterized the way in which Al-ions are bound to polymers of distearate. The Al is held by three acidic bonds arising from two carboxyl groups and a hydroxyl group, and by three coordinating bonds, two of which come from the carbonyl oxygens of carboxyl groups and one from a hydroxyl group. This may give an indication as to how Al-ions are bound in living tissue.

Anderson and Evans (1956) found that Al added to the reaction mixtures inhibited the activities of isocitric dehydrogenase and malic enzyme from the leaves of snap bean seedlings. Ragland and Berg² found extreme inhibition of pyruvate kinase activity due to Al. Each of these findings may be artifacts, however, for it was shown in the experiment with pyruvate kinase that the added Al caused a marked decrease in the pH of the reaction mixture. Since the optimum pH for pyruvate kinase activity is greater than 7, whether the inhibition was due to Al or the lower pH of the reaction mixture was not established.

Roberts (1956, 1957, 1953) investigated the effect of Al on the activity of wheat leaf phosphatase with fourteen different substrates. Only when pyrophosphate was the substrate did Al reduce phosphatase activity. Ragland and Berg² studied the effect of Al in the substrate on the activity of acid phosphatases from corn roots, snap bean roots and wheat germ. The enzymes from each source were strongly inhibited. Since these reaction mixtures were initially pH 5.0, for the enzymes from the corn and bean seedlings, and 4.1, for the enzymes from the wheat germ, the added Al did little to lower the pH. Phosphoenolpyruvate was used as the substrate for the corn and bean root phosphatases, and para-nitrophenylphosphate for the wheat germ phosphatases.

²J. L. Ragland and W. A. Berg. Unpublished data. Soils Department, North Carolina State College.

Horecker, et al. (1939) investigated the activation of succinic dehydrogenase-cytochrome system by Al. They showed that Al in very small concentrations accelerated aerobic oxidation of succinate. Trivalent chromium would substitute, but none of the divalent cations nor ferric iron would. Potter and Schneider (1942) made an extensive study of the effects of Al and Ca on this system. They concluded that the observed loss in succinic dehydrogenase activity, which occurred when liver was homogenized and diluted, was a multiple dilution effect caused by dissociation of cytochrome c, Ca and Al from succinic dehydrogenase and cytochrome oxidase.

Exchangeable and Soil-Solution Aluminum

Exchangeable Al. Attempts by early workers to assess soil acidity by titrations of water extracts of soils proved to be of little value. Only an insignificant part of the total soil acidity was measured by such a procedure. To overcome this difficulty, Hopkins, et al. (1903) introduced the use of neutral salt solutions for extracting the acidity from soils. Such a procedure gave good estimates of the lime requirements of soils. Daikuhara (1914) (as cited by Hardy, 1926) observed the formation of precipitates when the salt solution extracts of acid soils were neutralized and found these precipitates to be mixtures of Al, Fe and Mn hydroxides. Veitch (1904) attributed the acidity of neutral salt extracts of soils to

hydrolyzed Al salts, which formed when the cation of the neutral salt replaced Al from the soil. Truog (1916) agreed with this view and noted an equivalence between the quantities of Fe and Al replaced and the amounts of the cation of the neutral salt which were held up.

Parker (1914) and Knight (1920) disagreed with this idea, and maintained, as did Kelley and Brown (1926), that neutral salts reacted with H-soil to give free acid, which dissolves Al compounds, thus accounting for the Al in the leachate. The possibility of displaced H-ions dissolving $\text{Al}(\text{OH})_3$ was investigated by Harward and Coleman³. They mixed $\text{Al}(\text{OH})_3$ with H-resin and leached the mixture with salt solutions. With rapid leaching, only small amounts of Al were found in the leachate.

Liesegang and Kappen (1922) (as cited by Paver and Marshall, 1934) maintained that part of the Al and Fe was present in the soil as exchangeable ions, and that the exchange acidity of a soil is due solely to the hydrolysis of these ions. Paver and Marshall (1934) found that Al-treated electro dialyzed clay did not adsorb Al-ions, indicating that the electro dialysis treatment had produced Al-saturated clay rather than H-saturated clay, as generally had been supposed.

³M. E. Harward and N. T. Coleman. Unpublished data. Soils Department, North Carolina State College.

Work since this time by Coleman and Harward (1953), Grim (1953), Harward and Coleman (1954), Low (1955), McAuliffe and Coleman (1955), Mathers (1956) and Aldrich and Buchanan (1958) has shown conclusively that electrolyzed clays are predominantly Al-saturated and that permanent homoionic saturation with H was impossible. Certain treatments yield clays which are near H-saturation, but these are unstable and tend to change rapidly toward Al-saturation unless held at a low temperature. Mathers (1956) found that clays with electrostatically-bonded exchangeable hydrogen are unstable, and decompose to yield silicic acid and sufficient Al, Mg or other lattice ions to counter the exchange spots initially occupied by H-ions.

Chernov, et al. (1956), who have studied the subject extensively, came to the conclusion that the exchange acidity of acid podzolized soils and chernozems is largely due to exchangeable Al. Coleman, et al. (1959) found vanishingly small quantities of H in neutral salt leachates of several southeastern subsoils, instead they found that practically all of the exchange acidity was due to Al. Even with acid-washed peat, only about 6 per cent of the H-ions held by the peat was exchanged upon leaching with 1N KCl. Coleman, et al. (1958), in a review article, stated that the majority of the ions removed from an acid soil by leaching with a neutral salt are Ca, Mg, Al, K and H. Of these ions, the first three account for 90 per cent or more of the total ions replaced;

the proportions of Ca and Mg are largest on slightly acid soils; Al is the major exchangeable ion in many strongly acid soils.

The available literature strongly indicates that the exchange acidity of acid soils, particularly subsoil horizons, is due mainly to Al-ions exchanged into solution by the leaching cation. When in solution, part of the Al-ions hydrolyze to produce the observed H-ion concentration. Examination of some of the earlier work indicates that Al-ions are held in acid soils as exchangeable ions. Miyake, et al. (1924) showed that CaSO_4 was more effective than K_2SO_4 , which in turn was more effective than Na_2SO_4 , in putting Al into soil solution. This is the normal order of the replacing powers of these cations. Application of 0.5 and 2 tons per acre of gypsum to the acid Mardin silt loam increased the concentration of Al in the soil solution from 0.56 to 0.82 to 1.19 ppm, respectively, with an accompanying decrease in pH from 4.8 to 4.65 to 4.40 (Fried and Peech, 1946). Mathers (1956) studied the Al replacing power of the common cations and the replacing power of Al for these cations. He found that the adsorption affinities of the various cations on Kamec kaolin and Utah bentonite were: $\text{Al} \gg \text{Ca} > \text{K} > \text{H} > \text{Na}$.

With recognition of the existence of exchangeable Al in acid soils, it becomes important to relate the quantities of exchangeable Al to the concentrations, more specifically the

activities, of these ions in the soil solutions. Since natural soils have wide ranges of ion saturations, it is necessary to study ion exchange over the whole gamut of exchanger phase compositions. This was accomplished by Faucher and Thomas (1954), and Gaines and Thomas (1955) in studying Cs-Sr and Cs-K exchange on montmorillonite. Amphlett and McDonald (1956), using the methods of Thomas and co-workers, studied Cs-Sr exchange on montmorillonite and lower Greenland soil. As was found by Thomas and co-workers, the apparent exchange constant varied with the ion saturation, the exchange capacity, the solution concentration and the type of exchanger. Nye⁴ determined the adsorption isotherm for the exchange of K and Al on kaolinite. There was greater than one-hundred-fold variation in the apparent exchange constant with varying ion saturations of the exchanger phase. The results of these workers demonstrate the fallacy of the exchange constant concept and stress, rather, the necessity for determining selectivity coefficients (or apparent exchange constants) measured over the whole range of ion saturation.

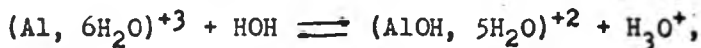
Forms of Al in soil solutions. There was relatively early interest in the nature of the Al in salt-extracts of acid soils. Dialysis of the soil extracts was one means used to investigate this. Knight (1920) placed the KNO_3

⁴P. H. Nye. The determination of the adsorption isotherm for the exchange of potassium and aluminum on kaolinite. Unpublished manuscript, Soils Department, North Carolina State College, 1958.

extract of an acid soil in a collodion sack and dialysed against water. He found that 74 per cent of the titratable acid had passed through the membrane. Upon neutralization, a heavy precipitate formed in the solution left in the sack, but the dialyzate remained clear. From this he concluded that Al was present in the KNO_3 extracts as non-acidic colloidal $\text{Al}(\text{OH})_3$, and that all of the acidity in the system was due to H-ions. Denison (1922) supported this conclusion. McGeorge (1924) also found that most of the titratable acidity in KNO_3 and H_2O extracts of acid soils passed out of dialysis sacks, but showed that it was Al- instead of H-ions. He did this by measuring Fe and Al in the extracts before and after dialysis. So long as the pH of the extract was less than 5.5, he found a great reduction in the amount of Al present in the sack after dialysis. From this he concluded that below this pH 5.5, most of the Al was in an ionic form. Knight (1920) and Denison (1922) had only measured the base required to neutralize the dialyzate and assumed, because no visible precipitate formed, the base had reacted with H-ions. Hardy (1926) criticized the use of dialysis for studies of this kind, on the basis that membranes may induce precipitation.

When soluble Al salts are dissolved in water, part of the Al-ions hydrolyze to yield hydroxy-aluminum ions and hydronium ions. This reaction causes a decrease in solution pH which is proportional, over a certain range, to the Al concentration.

Schofield and Taylor (1954) calculated, from pH measurements, the hydrolysis constant for the reaction:



and found it to be 4.98 at 25°C. They considered the concentration range from 2×10^{-5} to 10^{-2}M , which gave, at 25°C, a pH range from 5.06 to 3.68. The hydrolysis equation, as formulated above, represents the first stage of the hydrolysis of an Al solution. If the pH of the solution is raised, as by the addition of alkali or alkaline earth hydroxides, the reaction goes further until $\text{Al}(\text{OH})_3$ results.

Apparently the neutralization reaction does not go in a definite stepwise manner to give $\text{Al}(\text{OH})^{++}$, $\text{Al}(\text{OH})^{+}_2$ and then $\text{Al}(\text{OH})_3$ as has been imagined. Instead, the partially or completely neutralized Al-ions clump together to form aggregates which, when sufficiently large, form a visible precipitate. Aggregation begins as soon as the addition of base begins. Jahr and Brechlin (1952), (as cited by Ruff and Tyree, 1958), found the average number of Al atoms per aggregate to be a continuous function of the amount of base added, varying from 1 to 9.2 before precipitation of the hydrous oxide occurred. Sillen (1954), (as cited by Ruff and Tyree, 1958), suggested that $\text{Al}_6(\text{OH})_{15}^{+3}$ was the most important species of aggregate over the entire range of OH/Al ratios. Ruff and Tyree (1958) studied the kinds of aggregates formed with OH/Al ratios of 0 to 2.25 using a concentration range of 0.1 to 1.0M. They used a light-scattering technique to

determine the size of aggregate. The use of this technique is limited to solutions of about $0.1M$ or greater⁵. They found that the average molecular weight of the aggregates ranged from 138 to 1430 for 0 and 2.25 OH/Al ratios, respectively.

A point from Ruff and Tyree's work which seems very significant in considering the pH at which Al will precipitate was the effect of Al concentration upon the size of aggregates at a given OH/Al ratio. Their data indicate that the more dilute the solution the higher must be the OH/Al ratio for visible precipitation to occur. This sort of thing may have been responsible for the conclusion of Knight (1920), that no Al passed from the dialysis cell into the solution because no visible precipitate formed upon neutralization.

Another significant part of Ruff and Tyree's work was the observation that the precipitate which formed when the OH/Al ratio was 1.5, dissolved upon shaking for ten minutes. They interpret this as being due to reaction of unprecipitated Al species with the precipitate, producing large but soluble aggregates. These aggregates are thought then to undergo an extensive number of solution and re-aggregation reactions which tend to yield, with sufficient time, $Al(OH)_3$ aggregates and Al-ions⁵. Evidence by Lin and Coleman⁶ tends to support

⁵Personal communication from S. Y. Tyree, Chemistry Department, University of North Carolina.

⁶C. Lin and N. T. Coleman. Unpublished data. Soils Department, North Carolina State College.

this idea. They found that a clear solution of NaOH and AlCl_3 , $\text{OH}/\text{Al} = 2$, formed a precipitate after standing at room temperature for six months. The precipitate gave an intense gibbsite peak upon X-ray analysis. Upon water-dialysis of a portion of the resulting suspension, it was found that one-third of the Al was dialyzable, two-thirds was not. This indicates the reaction:



It is not known if the mechanism of hydrolysis and the hydrolysis products are the same in soil solutions as in pure solutions. Raupach (1957) concluded that Al^{+++} , $\text{Al}(\text{OH})^{++}$ and $\text{Al}_3(\text{OH})^+_8$ ions are possible in soil solutions below pH 7. Raupach (1955) found evidence for the existence of $\text{Al}_3(\text{OH})^+_8$ ions in the pH range 5.3 to 6.8. Tanabé (1954), (as cited by Raupach, 1957), reported the occurrence of this ion between pH 5 and 6 when AlCl_3 was titrated with base.

Rich and Obenchain (1955) concluded that precipitation of Al as hydroxy-Al was responsible for the failure of clay, from the A horizon of the Nason silt loam, to collapse upon K-saturation. The CEC of this material was greatly increased by treatments which solubilized hydrolyzed Al. Klages and White (1957) report extensive occurrence of a non-collapsing mineral in Indiana soils; its non-collapsing nature being due to interlayer hydroxy-Al or $\text{Al}(\text{OH})_3$. Whether the hydrolyzed interlayer Al comes from solution Al or Al countering exchange sites is not clear.

Anions other than OH will precipitate Al from soil solutions. Miyake, et al. (1924) found the order of precipitating power of phosphate and silicate anions to be $\text{HPO}_4 > \text{H}_2\text{PO}_4 > \text{SiO}_3$. Line (1926) found that aluminum phosphate precipitated from an aqueous mixture of $\text{Al}_2(\text{SO}_4)_3$ and KHPO_4 , at about pH 3.5.

Anions such as citrate and acetate do not precipitate Al, but instead form complexes with it which remain in solution at pH's of 7 or greater. The tendency of organic anions to complex Al may be responsible for reports which indicate that manure is effective in overcoming Al toxicities, the idea being that Al-ions which are complexed would not be free to react with plant tissue. Fatchikina (1953) found that 40-60 tons of manure per hectare, along with small amounts of lime, were as effective in overcoming Al-toxicity in a peaty-gley soil as were 10-20 tons of lime per hectare alone. The soil contained 12 meq. exchangeable Al per 100 g. Work by Butler (1957) indicated that organic matter will complex Al. The reactive groups responsible for binding Al were thought to be chiefly carboxylic.

ROOT GROWTH INTO ACID SUBSOILS

Exchangeable and Solution-Al Effects

Introduction

Six small greenhouse experiments were conducted, with the general objectives of finding the extent to which plant roots would grow into sub-surface layers taken from various Piedmont and Coastal Plain soils, and the influence, if any, of lime and fertilizer on root growth. Four of the experiments were quite similar, and consisted of growing plants in pots containing two layers of soil. The bottom layer was subsoil material, which may or may not have been given a lime or fertilizer treatment, while the upper layer was Norfolk sandy loam, A_p horizon. At harvest time, roots were washed from the soil, dried and weighed. Plant leaves also were dried and weighed, and in one experiment were analyzed for Ca.

The two other plant growth experiments dealt with the effects of electrolyte on root growth and on concentrations of Al in soil solutions. One was performed with potted soil, the other with suspensions of clay.

While the experiments to be described in the following section were similar in many respects, brief descriptions of each will serve well to introduce the particular work which was done. For this reason, the general descriptions of the soils used in each experiment, along with the pertinent details peculiar to that experiment alone, are included as

prefaces to the description of the results. Only general analytical matters common to all experiments are considered in the Methods section.

Methods

A variety of chemical methods were employed in characterizing the soils used in the various plant growth experiments to be described in the following sections. Most of these were aimed at finding various components of cation exchange capacity and their cation saturations.

To determine the permanent charge component of cation exchange capacity (CECp), and at the same time to determine exchangeable H and Al countering this, a method had to be devised. The one which follows was used:

1. Pack 0.5 g of filter paper pulp into the bottom of a small glass filter tube.
2. Mix 5 g of soil with 3 g of filter paper pulp and loosely pack into filter tube.
3. Pack 0.5 g of filter paper pulp on top of this and cover with a disc of filter paper.
4. Weigh the filled tube.
5. Leach with 50 ml. 1N NaCl and then two or three 5 to 10 ml. portions of H₂O.
6. Titrate the leachate with NaOH to the methyl-orange endpoint for a measure of exchangeable H and then to the phenolphthalein endpoint for a

measure of exchangeable Al.

7. Leach the soil-paper pulp mixture with 100 ml. 0.01N $MgCl_2$ and collect the leachate.
8. When the tubes have stopped dripping, weigh.
9. Titrate the $MgCl_2$ leachate with 0.02N Na_2 EDTA using Eriochrome Black T. indicator.

The CECp of the soil was calculated by:

$$CECp/5g = \text{meq. Mg added} - \text{meq. Mg in pore volumes} - \text{meq. Mg in leachate.}$$

The difference in weight of the wet and dry tubes times the normality of the added $MgCl_2$ equals the meq. Mg in pore volumes.

Exchangeable Ca, Mg and K were determined by the procedure which follows:

1. Mix 20 g of soil with 25 ml. 1N NH_4Cl and allow to stand for thirty minutes.
2. Transfer to filter funnel and wash to give total leachate of around 100 ml.
3. Add 10 ml. of a saturated ammonium oxalate solution to the leachate to precipitate the Ca and Mg.
4. Add 1:2 NH_4OH until alkaline to phenol red and filter.
5. Wash with 1:20 NH_4OH and save filtrate for flame photometric determination of K.
6. Dissolve oxalate precipitate in 1N HNO_3 to give a

total volume of 20 ml.

7. Take to dryness carefully on hot plate.
8. Dissolve residue in 0.1N HCl, transfer with HCl-washing to a 50 ml. volumetric flask and make to volume.
9. Use 25 ml. of solution for Ca + Mg determination by Na₂ EDTA titration, using Eriochrome Black T. indicator.
10. Use remaining solution for flame photometric determination of Ca.

In some cases CECp was taken as the sum of exchangeable cations instead of measuring CEC by the MgCl₂ method. The rather disturbing observation was often made that the sum of exchangeable cations exceeded the CECp determined by the MgCl₂ method. This discrepancy was taken to indicate a small amount of electrolyte uptake by the soil.

Where pH 8 CEC values are reported, these were obtained by adding the meq. of NaOH required to titrate a soil sample, in a neutral salt solution, to pH 8 to the meq. of exchangeable Ca, Mg and K. The NaOH was assumed to go for neutralization of H and Al countering CECp and for H ionized from pH-dependent exchange spots. The titration was carried out in a neutral salt solution in order to speed up the titration.

A number of measurements were made to determine soil acidity. Besides considering the sum of exchangeable H and Al, the soil pH in H₂O, in 1N KCl and in 0.001M CaCl₂.

was measured. A procedure often followed was to read the pH of 10 g soil in 10 ml. H_2O , add 10 ml. $2N$ KCl , stir and read it again. This procedure gave a pH measurement free of suspension effects and, by the difference in pH's, an estimate of the exchange acidity. The soil pH in $0.001M$ $CaCl_2$ was measured in order that "ratio law" pH's could be calculated (Schofield and Taylor, 1955).

The procedure followed to determine the Ca content of the plant was to dry-ash the plant material, take the residue up in 5 ml. of $1N$ HNO_3 , dilute to 25 ml. with $0.1N$ HNO_3 , add 5 ml. of saturated ammonium-oxalate, neutralize with 1:2 NH_4OH , allow to stand for thirty minutes, centrifuge for five minutes, discard the supernatant liquid, dissolve the precipitate in 5 ml. of $0.5N$ HNO_3 , dilute to 25 ml. and read on the flame photometer.

Soil-solution extracts were made by bringing the soil to saturation, allowing it to equilibrate for an hour or more and filtering in a large Buchner funnel. The concentrations of Al in saturation extracts of soils and the supernatants from clay suspensions were determined by a modified procedure described by Jones and Thurman (1957).

The essentials of the procedure are:

1. Pipet an aliquot of the solution, containing less than 7 ppm Al, in a 50 ml. volumetric flask.
2. Add 5 ml. of "Morgan's" extracting solution.
3. Add 2 ml. of iron-compensating solution.

4. Add 10 ml. of 0.5 per cent sodium thioglysolate.
5. Add 5 ml. of 0.075 per cent Eriochrome Cyanine R. and mix thoroughly.
6. Add 10 ml. of pH 6.0 ammonium acetate solution and dilute to volume.
7. Read at 535 $m\mu$ within fifteen to twenty minutes after addition of the Eriochrome Cyanine R.

Results

The effects of lime, fertilizer, phosphate and gypsum on root growth. The first experiments, regarded as exploratory, were performed with material taken from the B₂ horizon of an Orange soil, from Alamance County, North Carolina. The CECp of this material was 7.2 meq. per 100 g, and the soil contained 5.1 meq. of exchangeable Al per 100 g. Bulk samples of the material were mixed with amounts of CaCO₃ and MgCO₃ (2:1 equivalent ratio) to neutralize or to twice-neutralize the exchangeable Al, and with 0.1 per cent by weight of a soil conditioning polyelectrolyte (vinyl acetate-maleic acid co-polymer). The samples were then wet to field capacity and stored moist for two weeks. One-gallon pots were half filled with unlimed soil, or with that treated with 1 or 2 times CECp of lime. Where used, N, P and K were applied as NH₄NO₃, Ca(H₂PO₄)₂ and KCl at rates of 100, 85 and 85 parts per two million, respectively. Some of the unlimed soil was treated with 600 parts of P₂O₅ per two

million as $\text{Ca}(\text{H}_2\text{PO}_4)_2$, another sample was mixed with gypsum at the rate of 1200 parts per two million.

The subsoil treatments were arranged to examine the effects of lime alone, fertilizer alone, lime plus fertilizer, heavy phosphate application, and gypsum on root growth. Layers of Norfolk sandy loam surface soil were placed over the subsoil layers, and ten barley seeds (Hordeum vulgare) were planted in each. After four weeks, the plant tops were removed, the soil layers were separated, and roots were washed from each. The treatments, along with the results, are shown in Table 1 as averages of duplicates.

Neither fertilizer, a high rate of phosphate, or gypsum was very effective in promoting the growth of barley roots into the subsoil material. Root growth was increased about six-fold when lime, at the rate of 2.5 tons per acre, was added to the subsoil. No increase over the 2.5 ton rate of lime resulted from the application of 5.0 tons. Lime plus fertilizer gave only slightly better growth than lime alone, thus indicating that N, P and K were not seriously limiting root growth in this subsoil. The high rate of phosphate, a treatment which has repeatedly been shown to promote plant growth in acid soils, did little to increase root growth. The failure of gypsum to increase root growth discounts the possibility of low concentrations of Ca in the substrate as the cause for limited root growth. Lime was singularly effective in promoting vigorous root growth, its beneficial

effect was interpreted to be that of converting toxic Al to $\text{Al}(\text{OH})_3$ by raising the soil pH.

There was a striking decrease in the quantity of roots found in the topsoil layers where root growth in the subsoil layers was at a maximum. As a result of this, the sum of root growth in the two soil layers was not greatly different regardless of treatment. An adequate reason for this cannot be given, unless perhaps there is an inherent tendency of plants to grow a fairly constant quantity of roots for a certain amount of top growth.

Table 1. Effect of subsoil lime, fertilizer, high phosphate rate, and gypsum on the growth of barley roots into layers of Orange subsoil and Norfolk topsoil overlying the subsoil

<u>Treatment</u>	<u>Root growth (g/pot)</u>		
	<u>Subsoil layer</u>	<u>Topsoil layer</u>	<u>Sum</u>
Check	0.30	2.05	2.35
Fertilizer alone	0.80	1.20	2.00
High phosphate	0.50	1.90	2.40
Gypsum	0.30	2.15	2.45
2.5 T. lime	1.90	0.90	2.80
2.5 T. lime + fert.	2.05	1.90	2.70
5.0 T. lime	1.80	0.85	2.65
5.0 T. lime + fert.	2.15	0.60	2.75

Since root growth into the acid Orange B-horizon material was inhibited almost completely in the absence of lime, similar experiments were conducted with other subsoil materials of different CEC's and quantities of exchangeable Al.

Root growth in subsoil material from various North Carolina soils. Material from Norfolk, Portsmouth, Cecil, Rains, Creedmoor and White Store soils was used in this experiment. The Norfolk subsoil material was taken from the Research Farm at Clayton, North Carolina, the Portsmouth from the Tidewater Research Farm near Plymouth, North Carolina, the Cecil from a road bank near Crabtree Creek south of U. S. Highway 70 in Wake County, North Carolina, the Rains from near Burgaw, North Carolina, and the Creedmoor and White Store from a road bank on U. S. Highway 64 near Pittsboro, North Carolina. The pH's of the untreated Norfolk, Portsmouth, Rains, Creedmoor and White Store subsoils in 1N KCl, 1:2 soil-solution ratio, were 4.3, 4.2, 3.6, 3.4 and 3.1, respectively. The quantity of NaOH required to bring the Norfolk, Portsmouth, Cecil, Rains, Creedmoor and White Store subsoils to pH 7.0 when titrated in 1N KCl was 2.0, 10.3, 3.8, 7.3, 4.4, and 22.0 meq. per 100 g, respectively.

Two soil treatments were used in this experiment. They were: 1) sufficient lime to equal titratable acidity; and 2) no lime. Calcium oxide and $MgCO_3$ (2:1 equivalent ratio) were mixed with 500 g portions of the subsoils as required, placed in quart-size polyethylene freezer cartons, brought to field capacity, and allowed to equilibrate for a week. The containers, which were then about half full, were filled with Norfolk sandy loam topsoil, and ten barley seeds planted in the topsoil. The experiment was performed in duplicate.

A dilute nutrient solution containing N, P and K was added several times throughout the growing period, which lasted for thirty-nine days. At the end of this time the top growth was removed and the two soil layers separated. Roots were washed from each layer, oven-dried and weighed.

Table 2 shows the growth of barley roots into limed and unlimed layers of the six subsoils (averages of duplicates); also listed is the pH in 1N KCl of the unlimed materials. There was an obvious correlation between root growth and the initial pH of the unlimed subsoil layers. Roots grew into the Cecil subsoil, pH 4.6, in amount of 0.7 g per pot, but no roots grew into the White Store subsoil layer, pH 3.1. With the exception of the Cecil, the percentage increase in root growth due to liming was largest where soil acidity had been greatest.

Even though no lime was added to the Norfolk topsoil, overlying each subsoil layer, the addition of lime to the subsoil had its effect on the quantity of roots growing in the topsoil. In each case, liming the subsoil decreased root growth in the topsoil layer by roughly 50 per cent. In accordance with the results of the previous experiment, this caused the sum of root growth in the two layers of soil to be approximately equal regardless of liming treatment.

From the results of this experiment, it appears that the growth of barley roots into many subsoils of North Carolina could be increased by the addition of lime to the subsoils.

Table 2. Effect of subsoil liming on the growth of barley roots into subsoil layers and in Norfolk topsoil overlying the subsoils

Subsoil	Root growth (g/pot)						
	Subsoil			Topsoil		Sum	
	pH 1N KCl 1:2	No Lime	Limed	Unlimed Subsoil	Limed Subsoil	No Lime	Limed
Norfolk	4.3	0.46	0.63	0.88	0.40	1.34	1.03
Portsmouth	4.2	0.49	0.70	0.79	0.63	1.28	1.33
Cecil	4.6	0.70	1.36	0.40	0.34	1.10	1.70
Rains	3.6	0.08	0.97	1.54	0.72	1.62	1.69
Creedmoor	3.4	0.04	0.91	1.68	0.48	1.72	1.39
White Store	3.1	0.00	0.80	1.12	0.59	1.12	1.39

Effect of percentage neutralization of subsoil acidity on root growth. The possible existence of a critical base status of soil below which Al limits root growth was studied in other topsoil-subsoil layer experiments. The Rains, Creedmoor and White Store described in the previous experiment were used. The three subsoils were not used in a single experiment; rather, studies with each comprised separate experiments.

Calcium oxide and $MgCO_3$ (2:1 equivalent ratio), sufficient to neutralize 0, 20, 40, 60, 80 and 100 per cent of the titratable acidity, pH 7, was mixed with 500 g portions of the subsoils as required. Since it was suspected that the poor physical condition and the low natural fertility of the Creedmoor and White Store subsoils might limit root growth, soil conditioning polyelectrolyte (VAMA) in amount of 0.1 per cent of the soil weight, and 30 ppm N, 50 ppm K and

500 ppm P were mixed with the soil prior to the addition of the lime. The treated subsoils were placed in quart-size polyethylene freezer containers, brought to field capacity and allowed to equilibrate for two weeks. The remaining container volume was filled with 500 g of the standard Norfolk topsoil and fifteen barley seeds planted. A dilute nutrient solution containing N, P and K was used as needed to keep the plants growing vigorously. At the end of one month the top growth was removed, the layers of soil separated, and the roots washed from each. Soil samples were taken for pH measurements. Although the treatments, test crop and growing conditions were approximately the same, the time at which each subsoil was tested was different. The results were consolidated because of the close similarity of the three experiments. Each experiment was performed in duplicate and the results are presented as averages of these.

No roots grew into the Rains subsoil layer until 40 per cent of the soil acidity had been neutralized (Table 3). Maximum root growth occurred at 80 per cent neutralization, which corresponded to a subsoil pH of 5.8 in H_2O and 5.4 in 0.5N KCl. Where root growth was seriously limited, the roots were thickened and discolored, which are symptoms indicative of Al toxicity. Root growth was maximum in the topsoil layer where no lime was added to the subsoil. It then decreased and subsequently increased with increased additions

of lime to the subsoil. No explanation can be offered for this.

Table 3. Effect of percentage neutralization of subsoil acidity on the growth of barley roots into layers of Rains subsoil and overlying Norfolk topsoil

Percentage neutralization of acidity, pH 7	Subsoil pH		Root growth (g/pot)		
	H ₂ O	0.5N KCl	Subsoil	Topsoil	Sum
	1:1	1:2			
0	4.3	4.1	0	0.64	0.64
20	4.7	4.3	0	0.26	0.26
40	5.0	4.6	0.06	0.20	0.26
60	5.3	4.9	0.24	0.34	0.58
80	5.8	5.4	0.32	0.38	0.70
100	6.5	6.3	0.26	0.48	0.74

Root growth in the White Store and Creedmoor subsoil layers increased with increasing percentage neutralization of soil acidity (Table 4). With the White Store subsoil maximum growth occurred at 100 per cent neutralization, and at 60 per cent neutralization with the Creedmoor subsoil. The high percentage neutralization necessary for maximum root growth with the White Store may be due to zones of unneutralized acidity, which may have caused Al toxicity even though gross measurement of soil pH indicates the acidity to be too low for Al toxicity. Certainly such an occurrence would be more likely with a White Store subsoil, than with soils of much lower exchange capacities. The White Store subsoil contained 21 meq. exchangeable Al per 100 g.

Table 4. Effect of percentage neutralization of subsoil acidity on the growth of barley roots into White Store and Creedmoor subsoils and into overlying Norfolk topsoil

Percentage neutralization of acidity, pH 7	Subsoil pH		Root growth (g/pot)		
	H ₂ O	1N KCl	Subsoil	Topsoil	Sum
	1:1	1:2			
White Store					
0	4.4	3.6	0.07	1.21	1.28
10	4.5	3.6	0.02	1.32	1.34
20	4.9	4.0	0.14	1.17	1.31
40	4.9	4.0	0.43	1.05	1.48
60	5.1	4.1	0.67	0.86	1.63
80	5.6	4.6	0.73	0.87	1.60
100	5.8	4.7	0.91	0.82	1.73
Creedmoor					
0	4.4	3.6	0.16	0.34	0.50
20	4.7	3.7	0.28	0.28	0.56
40	4.8	3.8	0.44	0.22	0.66
60	5.2	4.2	0.49	0.23	0.72
80	5.1	4.1	0.38	0.22	0.60
100	6.0	5.2	0.38	0.22	0.60
100 ^a	-	-	0.38	0.32	0.70
100 ^b	-	-	0.40	0.30	0.70

^aNo soil conditioner added

^bNo soil conditioner or subsoil fertilizer added

Root growth was not reduced by failure to apply soil conditioner to the Creedmoor subsoil, nor did the absence of soil conditioner and fertilizer reduce it (Table 4). Although increasing the quantity of lime added to the subsoil layers decreased root growth in the topsoil layers, as shown before, in these cases the sum of root growth in the two layers was somewhat increased.

Assuming that Al injury is the reason for poor root growth in these subsoil layers, the results of these

experiments show that lime sufficient to equal 60 to 100 per cent of the titratable acidity (pH 7) must be added before the activity of Al-ions is sufficiently low to prevent injury. The short, thickened, discolored roots, and indeed the failure of roots to grow at all in some subsoil layers where the percentages of neutralization were low, strongly suggests Al injury.

Root growth in Norfolk Catena subsoils. This experiment was designed to investigate the relations between root growth and chemical characteristics of the soils in the Norfolk Catena. Two profiles each of the Norfolk, Goldsboro, Lynchburg, Rains and Portsmouth soils were selected for the study. The exact location of each profile, all of which occurred in Duplin County, North Carolina, is recorded in the soil survey section of the North Carolina State College Soils Department. The soils in this Catena, which were formed in mixed unconsolidated sediments of sand and clay, range from Red-Yellow Podzolic to Humic Gley. The clay minerals are predominantly kaolins and interstratified three-layer silicates.

Bulk samples were taken with post-hole diggers from the A_p, A₂, B₂ and C₁ horizons of each soil. The pH, exchangeable cations, and cation exchange capacity of the various horizons are shown in Table 5.

Soil material from the B horizon of each soil sampled was used in an experiment to determine the effect of subsoil

Table 5. Chemical properties of two profiles each of the five soils in the Norfolk Catena

Sample Site	Soil Horizon	pH		Exchangeable cations						pH 8 ^a	
		H ₂ O 1:1	1N KCl 1:2	H	Al	Ca+Mg	Mg	K	Sum	CECp	CEC
3	N-A _p	5.2	4.7	0.06	-	0.56	0.00	0.12	-	1.54	2.58
3	N-A ₂	5.1	4.7	0.04	-	0.34	0.06	0.12	-	1.88	1.86
3	N-B ₂	4.7	4.4	0.20	0.58	0.84	-	0.27	1.89	2.38	6.41
3	N-C ₁	4.7	4.5	0.12	-	1.06	-	0.08	-	2.76	4.94
7	N-A _p	5.4	4.7	0.10	-	0.60	0.06	0.16	-	1.40	3.36
7	N-A ₂	5.2	4.8	0.08	-	0.37	0.15	0.15	-	1.08	2.02
7	N-B ₂	5.0	4.6	0.12	0.32	0.94	0.19	0.08	1.46	2.00	3.52
7	N-C ₁	4.9	4.7	0.04	-	0.56	0.16	0.03	-	1.56	2.99
2	G-A _p	5.5	5.2	0.00	-	0.52	-	0.12	-	1.66	2.24
2	G-A ₂	5.1	4.8	0.02	-	0.94	0.29	0.08	-	1.84	3.42
2	G-B ₂	4.7	4.5	0.08	1.08	0.94	0.51	0.04	2.14	2.18	3.58
2	G-C ₁	4.6	4.5	0.06	-	0.42	-	0.86	-	2.04	3.98
9	G-A _p	4.7	4.3	0.20	-	0.50	-	0.08	-	2.68	9.88
9	G-A ₂	4.7	4.4	0.08	-	-	-	0.04	-	2.06	-
9	G-B ₂	4.8	4.5	0.08	1.33	-	-	0.03	-	1.86	-
9	G-C ₁	4.8	4.6	0.06	-	0.20	-	0.03	-	1.84	3.03
1	L-A _p	4.8	4.7	0.04	-	0.74	-	0.12	-	2.20	4.46
1	L-A ₂	4.8	4.7	0.04	-	0.48	-	0.10	-	2.28	2.68
1	L-B ₂	4.6	4.5	0.06	1.03	0.88	0.27	0.04	2.00	2.08	3.62
1	L-C ₁	4.6	4.5	0.12	-	0.70	0.39	0.03	-	2.06	3.33

Table 5 continued

Sample Site	Soil Horizon	pH		Exchangeable cations							pH 8 ^a	
		H ₂ O 1:1	1N KCl 1:2	H	Al	Ca+Mg	Mg	K	Sum	CECp	CEC	
8	L-A _p	5.6	4.9	0.04	-	0.74	-	0.11	-	1.46	3.05	
8	L-A ₂	5.3	4.8	0.04	-	0.30	0.02	0.05	-	1.00	1.35	
8	L-B ₂	4.9	4.5	0.08	0.99	1.00	0.16	0.07	3.14	-	5.17	
8	L-C ₁	4.9	4.5	0.08	-	0.22	0.08	0.03	-	1.74	3.35	
4	R-A _p	5.2	4.7	0.06	0.54	3.25	0.82	0.05	3.90	3.36	9.20	
4	R-A ₂	4.9	4.5	0.06	1.72	2.05	1.32	0.03	3.86	3.28	6.58	
4	R-B _g	4.8	4.4	0.06	2.26	1.50	1.03	0.03	3.85	2.89	5.13	
4	R-C ₁	4.9	4.3	0.16	2.84	1.00	0.84	0.05	4.05	3.29	5.85	
10	R-A _p	4.7	4.3	0.08	1.94	2.80	0.80	0.22	5.04	4.19	16.42	
10	R-A ₂	4.8	4.6	0.16	1.61	1.30	0.27	0.08	3.15	1.97	6.28	
10	R-B _g	4.7	4.5	0.08	2.96	1.60	1.11	0.05	4.69	2.32	5.65	
10	R-C ₁	4.9	4.5	0.12	2.15	1.70	-	0.09	4.06	2.74	7.09	
5	P-A _p	5.1	4.5	0.32	0.86	5.10	0.23	0.12	6.40	6.55	-	
5	P-A ₂	4.5	4.3	0.36	4.84	2.10	-	0.05	7.35	6.40	10.85	
5	P-B _g	4.4	4.3	0.32	5.37	1.50	-	0.04	7.23	5.02	9.44	
5	P-C _g	4.5	4.4	0.20	4.62	1.20	1.25	0.04	6.06	4.55	8.74	
6	P-A _p	4.2	4.0	0.76	3.66	2.70	-	0.06	7.18	5.69	20.56	
6	P-A ₂	4.6	4.4	0.20	4.20	1.10	1.02	0.03	5.53	3.60	13.63	
6	P-B _g	4.7	4.7	0.12	3.28	0.90	0.62	0.02	4.94	2.95	8.72	
6	P-C _g	4.8	4.7	0.08	2.26	0.80	0.28	0.02	3.16	2.38	6.72	

^apH 8 CEC = meq. exchangeable K, Ca and Mg + meq. base required per 100 g to titrate the soil to pH 8.0

N-Norfolk f.s.l., G-Goldsboro f.s.l., L-Lynchburg f.s.l., R-Rains f.s.l., P-Portsmouth loam

acidity on root growth. Where lime was added, 500 g portions of the soils were mixed with quantities of CaO and MgCO₃ (2:1 equivalent ratio) sufficient to equal the exchange acidity to 1N KCl. The unlimed and limed soils were placed in paper containers, brought to field capacity, and allowed to stand for a week. Similar containers with the bottoms removed were set on top of the subsoil-filled containers. These were filled with 500 g of Norfolk topsoil, which received no lime or fertilizer during the course of the experiment. The pots were seeded to grain sorghum (Sorghum vulgura, var. Mardin) and watered with distilled water. After thirty days, the top growth was harvested, the two layers of soil separated, a soil sample taken from the subsoil layer, and the roots washed from each layer. The pH of the soil was measured in a 1:1 soil-water mixture, a 1:2 soil-1N KCl mixture and a 1:2 soil-0.001M CaCl₂ mixture.

The relation of root growth to various chemical properties of the unlimed subsoils is shown in Table 6 (average of duplicates). The subsoils are listed in the order of decreasing natural drainage. The growth of grain sorghum roots decreased from about 0.1 g dry weight per pot in the Norfolk subsoils, to no root growth in the Portsmouth subsoils. In comparing the meq. exchangeable Al in these two subsoils, there was about ten times as much Al in the Portsmouth as Norfolk subsoils. The soil pH in 0.001M CaCl₂

changes from about 4.65 to about 4.35 from the Norfolk to Portsmouth subsoils. The meq. exchangeable Ca+Mg/100 g remained fairly constant over the range of well- to poorly-drained soils. Figure 1 shows clearly the inverse relation of root growth to the exchangeable Al contents of the unlimed subsoils.

Table 6. Growth of grain sorghum roots into unlimed Norfolk Catena subsoil layers as related to the exchangeable cations of the subsoils

Soil site	Subsoil	g Roots per sub-soil layer	Exch. Al (meq./100g)	Soil pH $10^{-3}M$ CaCl ₂ 1:2	Exch. Ca+Mg (meq./100g)
3	Norfolk	0.086	0.58	4.60	0.84
7	Norfolk	0.130	0.32	4.70	0.94
2	Goldsboro	0.079	1.08	4.50	0.94
9	Goldsboro	0.052	1.33	4.35	-
1	Lynchburg	0.066	1.03	4.50	0.88
8	Lynchburg	0.084	0.99	4.65	1.00
4	Rains	0.022	2.26	4.40	1.50
10	Rains	0.010	2.96	4.35	1.60
5	Portsmouth	0.000	5.37	4.30	1.50
6	Portsmouth	0.002	3.28	4.40	1.10

The increase in soil pH and root penetration caused by the addition of lime to the subsoil layers is shown in Table 7. Again the interpretation is made that the added lime raised the pH of the soil and caused hydrolysis of soil-solution and exchangeable Al, thus the increased root growth. The relation of root growth to the pH of the soil

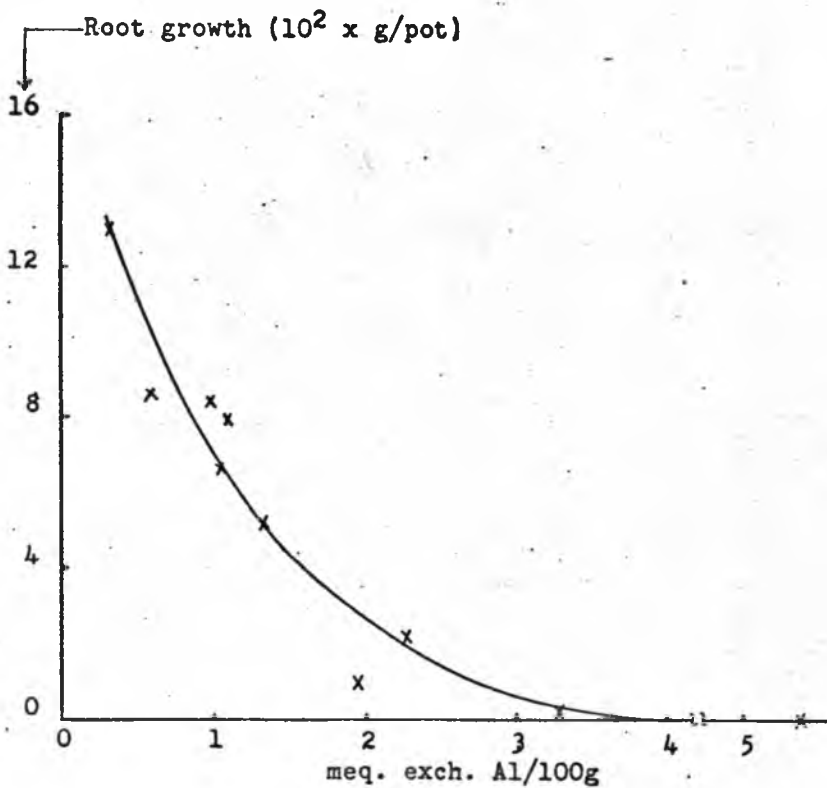


Figure 1. The growth of grain sorghum roots into unlimed subsoils of the Norfolk Catena as related to quantities of exchangeable Al present

for the unlimed and limed subsoils is shown in Figure 2.

The higher the pH, the more extensive was root growth.

Table 7. Effect of lime on soil pH and on the growth of grain sorghum roots into subsoils from the Norfolk Catena

Soil site	Subsoil	Soil pH		g Roots/subsoil layer	
		$10^{-3}M CaCl_2$; 1:2 Unlimed	Limed	Unlimed	Limed
3	Norfolk	4.6	5.0	0.086	0.380
7	Norfolk	4.7	5.2	0.130	0.214
2	Goldsboro	4.5	5.2	0.079	0.248
9	Goldsboro	4.4	5.1	0.052	0.174
1	Lynchburg	4.5	5.3	0.066	0.170
8	Lynchburg	4.6	5.3	0.084	0.286
4	Rains	4.4	5.3	0.022	0.281
10	Rains	4.4	5.4	0.010	0.184
5	Portsmouth	4.5	5.2	0.000	0.141
6	Portsmouth	4.4	5.3	0.002	0.224

The tendency for the sum of the root growth in the two soil layers to be equal in the absence and presence of lime added to the subsoil layers existed, although it was not so evident in this experiment as in the ones previously described.

The Ca contents of the plant tops grown in the absence and presence of limed subsoil layers are shown in Table 8. Although the dry weight of tops was unaffected by added lime, the Ca content of the tops was approximately doubled in each case. The Ca contents of the roots were not measured, but it was assumed that a similar increase was effected by the added lime.

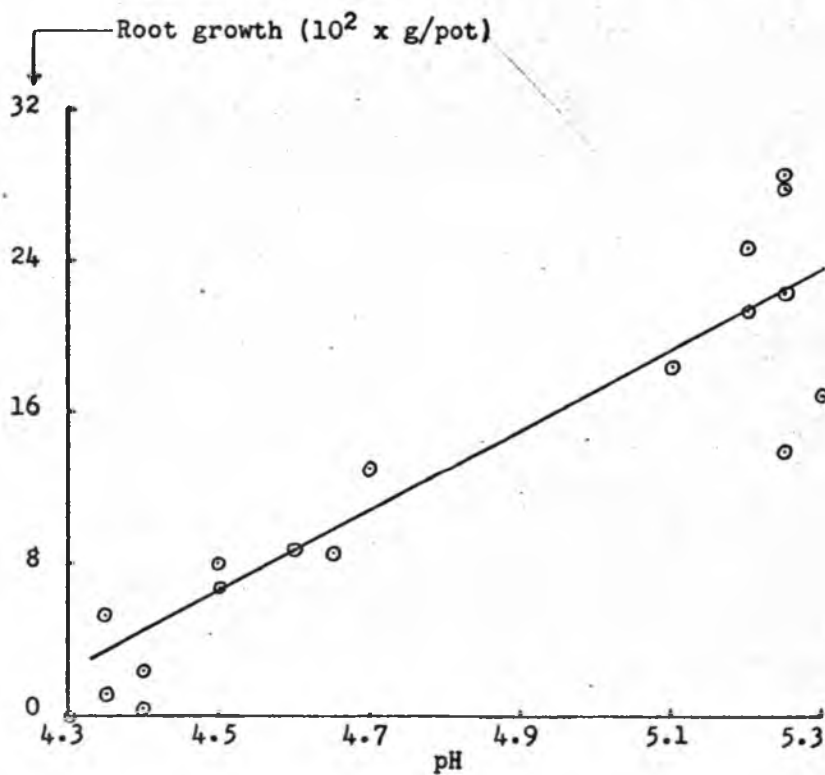


Figure 2. The growth of grain sorghum roots into subsoils of the Norfolk Catena as related to their pH in $0.001M \text{ CaCl}_2$

Table 8. Effect of subsoil liming on the growth and Ca content of grain sorghum tops

Soil site	Subsoil	Weight of tops (g/pot)		Ca content of tops (meq./g)	
		Unlimed	Limed	Unlimed	Limed
3	Norfolk	0.50	0.54	0.20	0.40
7	Norfolk	0.47	0.62	0.24	0.32
2	Goldsboro	0.56	0.60	0.18	0.30
9	Goldsboro	0.44	0.48	0.14	0.24
1	Lynchburg	0.54	0.48	0.18	0.30
8	Lynchburg	0.48	0.62	0.20	0.41
4	Rains	0.58	0.66	0.17	0.34
10	Rains	0.62	0.64	0.20	0.38
5	Portsmouth	0.56	0.48	0.13	0.25
6	Portsmouth	0.55	0.68	0.12	0.34

Whether the poor root growth in the absence of added lime was due to the low Ca content of the tissue cannot be ascertained from this experiment. If Ca were limiting, it was probably because of reduced uptake caused by Al injury to the roots, rather than low concentrations in the substrate. The failure of gypsum to increase root growth of barley with the Orange subsoil is cited in this regard (Table 2). Schmehl, Peech and Bradfield (1952) found that Al decreased Ca uptake by alfalfa. Burstrom (1954) has shown the dependence of root cell elongation upon substrate Ca. Although the evidence cited in the previous sections can be connected with such observations only in a circumstantial way, it is interesting to speculate on the possible importance of Ca-Al interactions

in controlling the growth of roots and certain aspects of their behavior.

Relation of root growth to the concentrations of Al and Ca+Mg in soil-solution extracts⁷. It could be supposed that Al in soil-solution is the effective form causing toxicity. To investigate this, root growth was correlated with quantities of Al in saturation extracts of soils in which the roots grew. Three soil materials, the B₂ horizons of Creedmoor and Appling and the A_p horizon of a Portsmouth soil, were used. The Appling is a Red-Yellow Podzolic soil from the Piedmont region, derived from mica gneiss and schist. The predominant clay mineral is kaolinite, though there are appreciable quantities of vermiculite. The Creedmoor soil is a Red-Yellow Podzolic soil derived from Triassic siltstone and shales. Montmorillonite-like and interstratified three-layer silicates are the predominant clay minerals in the upper horizons, the proportions of the former increasing with depth. The Portsmouth soil is a Humic Gley soil from the Coastal Plain formed in mixed unconsolidated sediments of sand and clay. The A_p horizon is relatively high in organic matter and the soil has a predominance of kaolins and interstratified three-layer silicates. Initial

⁷Appreciation is expressed to Dr. G. W. Thomas and W. Albert Berg for assistance in performing this experiment.

exchangeable Al contents were 5.00, 4.60 and 1.60 meq. per 100 g for the Creedmoor B₂, the Appling B₂ and the Portsmouth A_p.

The soils were treated with 0, 0.5 or 1 meq. of KCl and 0 or 3 meq. of lime per 100 g. It was expected that the added K would increase, by cation exchange, the concentration of Al in the soil solution, while the lime would reduce it. The treatments were made in factorial combination, using two replications. The treated soils were placed in number 10 tin cans and sweet corn (Zea mays) grown on them for four weeks. At the end of this period the tops were harvested and the roots dry-sieved from the soil. Saturation extracts were made of the soils on which the corn had grown: The concentrations of Al and Ca+Mg therein were measured. The water percentages at saturation, on a weight basis, were 25 and 22 per cent for the Creedmoor and Portsmouth soils, respectively, and 62 per cent for the Appling soil.

The percentages of maximum root and top growth of sweet corn and the concentrations of Al and Ca+Mg in saturation extracts from these soils are shown in Table 9. Results for the three soils are quite similar except for the Appling, which was, in its native state, quite high in exchangeable K. Also, the high water percentage required to saturate the Appling soil caused the ion concentrations in saturation extracts from this soil to be much lower than in the extracts from the Creedmoor and Portsmouth soils.

Table 9. The effect of KCl and lime on the concentration of Al and Ca+Mg in soil solutions and on the percentage of maximum root and top growth of sweet corn on Creedmoor, Portsmouth and Appling soils

Meq. Ca(OH) ₂ +MgO per 100 g Soil		Meq. KCl per 100 g soil		
		0	0.5	1.0
Creedmoor				
0	Roots	83	29	8
	Tops	74	53	20
	ppm Al	<.05	36	82
	meq. Ca+Mg/liter	0.60	7.0	7.4
3.0	Roots	48	86	100
	Tops	96	86	100
	ppm Al	<.05	0.48	4.0
	meq. Ca+Mg/liter	0.60	9.2	18
Portsmouth				
0	Roots	41	36	23
	Tops	23	29	29
	ppm Al	0.80	18	46
	meq. Ca+Mg/liter	0.50	3.0	4.0
3.0	Roots	23	100	98
	Tops	35	100	86
	ppm Al	0.20	0.20	0.80
	meq. Ca+Mg/liter	1.6	4.0	8.0
Appling				
0	Roots	91	82	61
	Tops	64	59	65
	ppm Al	<.05	<.05	0.9
	meq. Ca+Mg/liter	0.7	1.0	2.9
3.0	Roots	88	78	100
	Tops	70	100	77
	ppm Al	<.05	<.05	<.05
	meq. Ca+Mg/liter	1.2	3.3	9.8

Where no lime was added, increasing the quantity of KCl applied from 0 to 1.0 meq. increased the Al concentration in the soil solution from $<.05$ to 82 ppm for the Creedmoor soil, 0.8 to 46 ppm for the Portsmouth soil, and $<.05$ to 0.9 ppm for the Appling soil. Why there was a measurable concentration of Al in the soil solution from the untreated Portsmouth soil (0.8 ppm) is not clear, perhaps it was due to solubilization of Al by organic acids from the organic matter. The growth of grain sorghum roots was correspondingly decreased from 83 to 8 per cent of maximum for the Creedmoor, 41 to 23 per cent for the Portsmouth, and 91 to 61 per cent for the Appling.

Where 3.0 meq. of lime had been added, increasing the quantity of KCl applied did not increase very greatly the concentration of Al in the soil solution, but did increase root growth. The relation of root growth and solution concentrations of Al to KCl and lime treatments is shown in Figure 3. Top growth followed, in general, the same trends as root growth.

The reverse effects of added KCl in the absence and presence of lime appeared to be salt-induced Al toxicity in the former, and K response in the latter situation. The response to K is interpreted to be due to a Ca-induced K deficiency. Where no lime was added, K exchanged for Al and thus greatly increased the soil solution concentration of Al, which produced Al toxicity. In the presence of lime, the

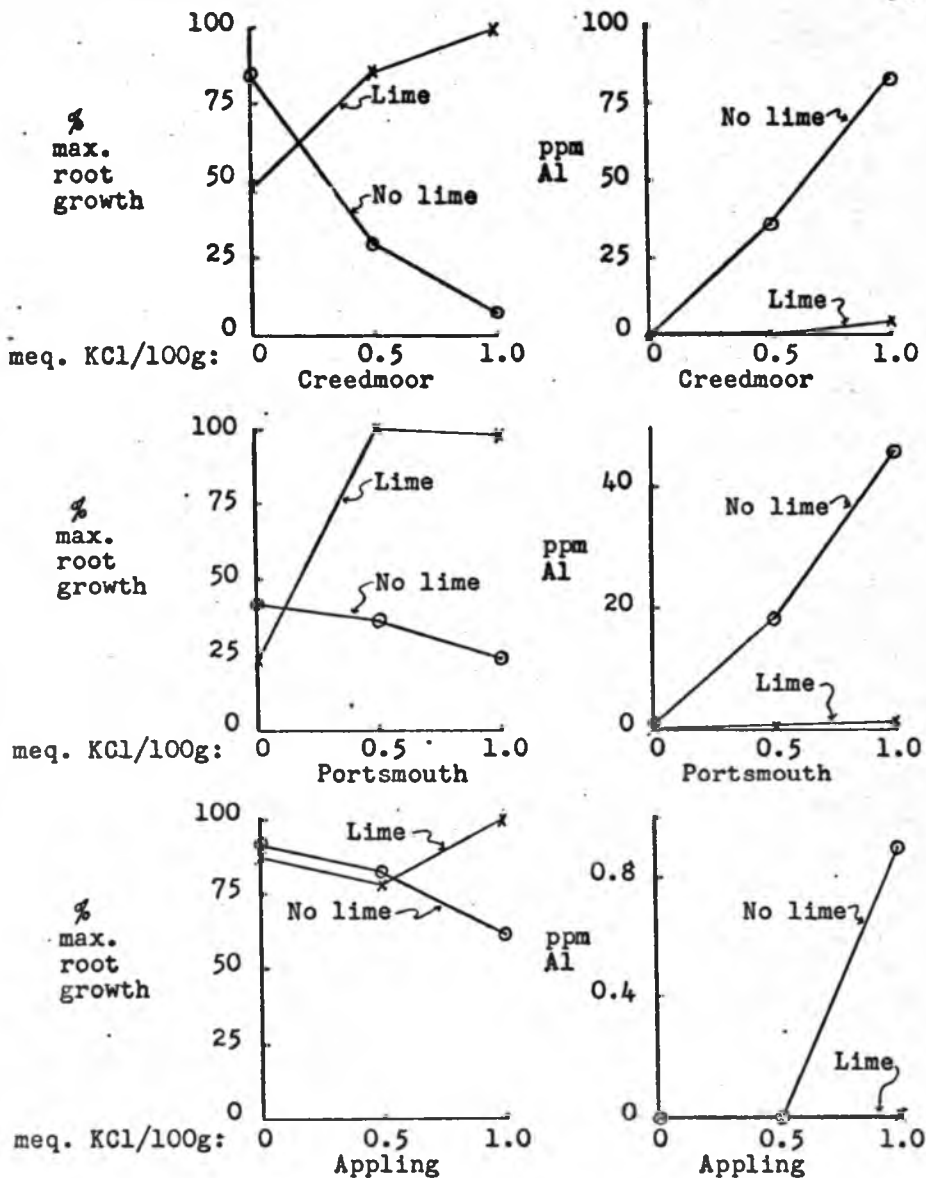


Figure 3. Effect of KCl and lime on root growth and concentrations of Al in soil solution extracts

higher pH caused precipitation of Al brought into solution by exchange with K.

In the unlimed soils, K increased, by exchange, the concentrations of Ca and Mg in the soil solutions, but because of the same effect on the concentration of Al, root and top growth was least where the concentrations of Ca and Mg were highest. This demonstrates clearly that acid soil injury is more involved than a simple deficiency of Ca in the soil solution.

Root growth in White Store clay suspensions varying in Ca-saturation and CaCl_2 concentration. The idea that Al in the soil solution is the toxic form was pursued further in an experiment to measure the effects of salt content and percentage neutralization of soil acidity on the growth of sorghum roots in White Store clay suspensions. The White Store soil is a Red-Yellow Podzolic soil derived from Triassic siltstone and shales. Montmorillonite-like and interstratified three-layer silicates are the predominant clay minerals in the upper horizons, the proportions of the former increasing with depth. In order to get a wide range of Al concentration in solution, three rates of CaCl_2 were imposed upon each of five levels of neutralization. The White Store clay was obtained by mechanically dispersing soil (no chemical dispersing agent being added) and separating the less than two micron material by sedimentation. The clay required 30 meq. base per 100 g for neutralization to

pH 6.0. Enough $\text{Ca}(\text{OH})_2$ was added to 350 ml. batches of the 1 per cent clay suspension to give 0, 10, 20, 40 and 80 per cent neutralization. The three rates of CaCl_2 employed were 0.1, 1.0 and 10.0 meq. per 100 g clay. The treated clay suspensions were placed in 400 ml. beakers, the tops of which were fitted with pieces of lacquer-covered hardware cloth, 1/4-inch mesh. The wire was covered with cheesecloth which extended down into the clay suspension. This arrangement allowed conduction of water to the seed for germination and growth. The clay was kept suspended in each beaker by an air stream passing through a sintered-glass aeration tube. The grain sorghum seeds, which germinated in about twenty-four hours, were allowed to grow for ten days, after which time the roots and tops were separated and the fresh weights determined.

The growth of grain sorghum roots in suspensions of White Store clay (average of duplicates) is shown in Table 10, expressed as g fresh weight per pot; also listed are the initial pH and solution concentrations of Al and Ca+Mg. Root growth was reduced by increased CaCl_2 at each neutralization level, even though the resulting concentration of Al in solution was often less than a measurable quantity (<.05 ppm). Only at the 80 per cent neutralization level was root growth not seriously reduced by increased CaCl_2 rates. Here sufficient $\text{Ca}(\text{OH})_2$ had been added to precipitate virtually all of the Al from solution. The failure of grain

sorghum roots to grow where Al concentrations were quite low, in comparison with some of the saturation extracts in the

Table 10. Effect of CaCl_2 and $\text{Ca}(\text{OH})_2$ additions to a 1.0 per cent White Store clay suspension^a on pH, Al and Ca+Mg^a in solution and on the fresh weight of 10 day old grain sorghum tops and roots grown in the suspension

	% Neutralization of soil acidity with $\text{Ca}(\text{OH})_2$, pH 6	Meq. CaCl_2 per 100 g clay		
		0.1	1.0	10.0
0	g tops	1.18	- ^b	- ^b
	g roots	0.15	- ^b	- ^b
	pH	4.8	3.9	3.5
	ppm Al	<.05	0.13	3.5
	Ca+Mg	<.01	0.13	0.36
10	g tops	2.37	3.46	2.38
	g roots	0.30	0.15	- ^c
	pH	4.9	4.1	3.6
	ppm Al	<.05	0.08	2.5
	Ca+Mg	<.01	0.13	1.6
20	g tops	2.96	3.14	2.84
	g roots	0.45	0.21	0.05
	pH	5.0	4.3	3.8
	ppm Al	<.05	0.06	1.7
	Ca+Mg	<.01	0.14	1.7
40	g tops	3.76	3.86	3.60
	g roots	1.9	1.4	0.2
	pH	5.2	4.6	4.0
	ppm Al	<.05	<.05	0.80
	Ca+Mg	0.01	0.17	1.8
80	g tops	3.64	4.02	3.97
	g roots	2.6	2.5	1.9
	pH	5.4	5.0	4.4
	ppm Al	<.05	<.05	0.17
	Ca+Mg	0.03	0.20	2.5

^aCa+Mg expressed as meq. per liter

^bNot measured

^cLess than a measurable quantity

previous experiment, was due to the greater sensitivity of sorghum to Al toxicity as contrasted to sweet corn. Top growth was not greatly different for any treatment except the 0 rate of lime; here growth was seriously reduced.

Discussion

The several two-layer experiments described in the preceding sections gave results with many common features. Generally, barley or sorghum roots did not grow well, if at all, into acid subsoils. Fertilization with N-P-K without lime did not improve root growth, nor did aggregate stabilization to improve physical characteristics. Lime and lime alone was an adequate ameliorating agent. Not only was liming of acid subsoils necessary to obtain root growth in them, but also the quantity of lime had to be sufficient to hydrolyze and precipitate nearly all of the exchangeable Al and to essentially satisfy the permanent charge component of CEC with basic metal ions. Although this does not prove that exchangeable and soluble Al-ions prevented the growth of roots into the acid subsoils, the circumstantial evidence is overwhelmingly in favor of the hypothesis that they did.

As indicated in the review of literature, rather small concentrations of Al-ions in nutrient solutions inhibit plant growth, particularly root growth. In soils, though deficiencies of Ca, Mg or Mo, or toxicities due to Mn, cannot be discounted completely, the large quantities of exchangeable

Al in many of the soils examined in this work lead one to suspect that Al toxicity might be one of the first limiting factors. Work of Pierre and his co-workers (1931), Vlamis (1953), and Mathers (1956) is pertinent in this regard, in that they all established Al toxicity as a primary cause for poor plant growth in acid soils. Mather's (1956) conclusions are of particular interest, since he worked with some of the same soils used in the experiments reported here. Through rather elaborate experiments, involving additions of CaCO_3 , MgCO_3 and CaSO_4 to soils and observing the effects on the growth, appearance and mineral content of plants, he was able to distinguish clearly between Ca-deficiency and Al-toxicity. With the Rains and Orange soils, Al toxicity was established as the major injurious effect of soil acidity; Al toxicity could be overcome only by adding appropriate amounts of lime or other neutralizing substances.

In the present study, the addition of lime in amounts sufficient to neutralize all of the permanent charge-acidity of an acid Orange subsoil increased root development over six-fold. Calcium deficiency, per se, was more or less eliminated by the fact that the addition of gypsum gave no response. Of course, adding a salt like CaSO_4 would intensify Al injury through increasing solution concentrations of Al, and responses to Ca added as a salt might be prevented by this. The failure of subsoil fertilization to increase root

development ruled out N-P-K deficiency as a first limiting factor. Even a "high" rate of phosphate (600 pp2m P_2O_5) did not increase root penetration. This might seem surprising, unless one takes into account that the quantity of exchangeable Al in the acid soil was equivalent to four times the amount of phosphate applied. Perhaps 2400 pp2m of P_2O_5 would have prevented the acid-soil injury; certainly 600 did not.

The two-layer experiments with six acid soils, all either in their native condition or with sufficient lime added to neutralize acidity, pH 7, showed the general occurrence of root-inhibition in subsoils and the fact that it can be overcome by liming. In addition, a general parallelism between the extent of injury and the magnitude of acidity, pH 7, was shown. Though some depression of root growth occurred with all of the acid subsoils, as shown by responses to lime, this was moderate for the Cecil, Norfolk and Portsmouth soils and was severe for the Rains, Creedmoor and White Store. This is exactly what would be expected if exchangeable Al were the toxic agent.

The work with partially neutralized Rains, White Store and Creedmoor soils further pointed out the general inverse relations between quantities of exchangeable Al and amounts of roots developed. The White Store, for example, had 22 meq. per 100 g of acidity, pH 7, of which about 18 meq. was Al. Root growth increased as the soil was limed, becoming

substantial after the addition of about 10 meq. of lime. At this point, with some 12 meq. of exchangeable Al left, root growth was about 60 per cent of maximum. With the Creedmoor and Rains soils, however, with smaller initial amounts of exchangeable Al, reduction to 2.2 and 1.8 meq. per 100 g, respectively, gave 60 per cent of maximum growth. This suggested that percentage Al saturation, rather than amount of exchangeable Al, per se, might be the critical factor. That such may be the case is indicated by Figure 4, which compares relative root growth with percentage Al-saturation. It appears that if Al saturation of CECp is larger than approximately 20 per cent, substantial reduction in root growth can be expected. As indicated in other experiments, however, the apparent "critical value" is, in fact, more apparent than real, and changes drastically with the electrolyte concentration of the soil solution.

Also included in Figure 4 are points obtained from the experiment with the soils of the Norfolk Catena. Generally, they lie below the line established by the percentage neutralization studies, indicating somewhat greater plant sensitivity to exchangeable Al than would be inferred from the data obtained with the White Store, Creedmoor and Rains. This emphasizes that it is a great oversimplification to speak of "critical values" for Al-saturation, but does not detract from the general concept that nearly complete saturation of CECp with basic cations is essential.

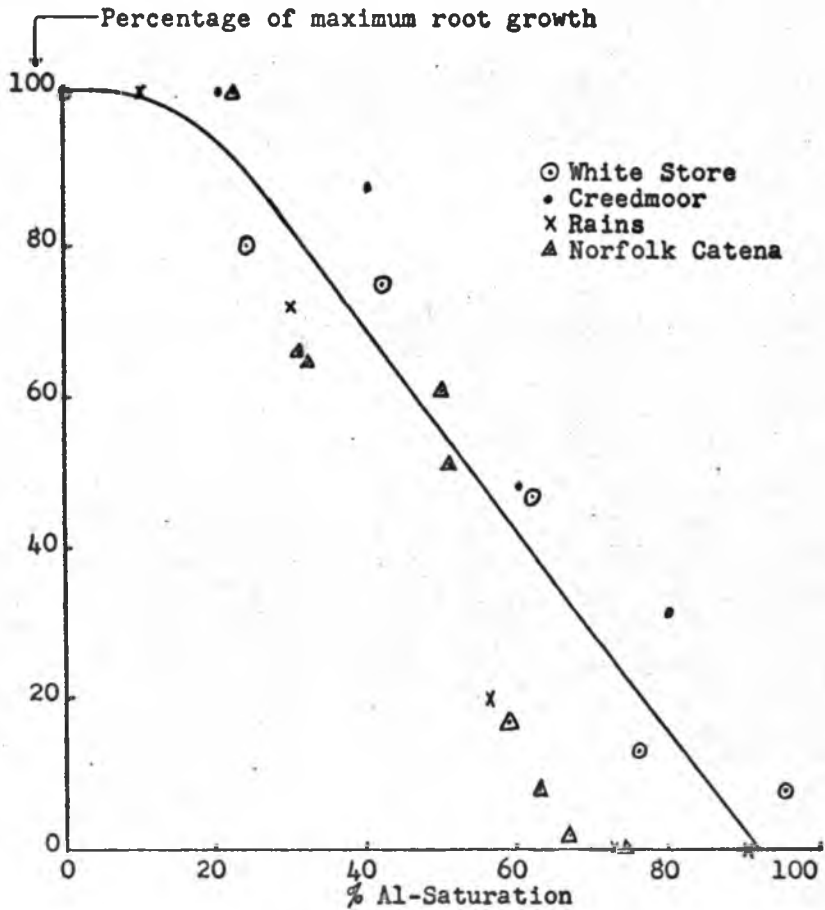


Figure 4. Relative root growth into White Store, Creedmoor, Rains and Norfolk Catena subsoils as related to the percentage of their CEC_p countered by Al

It seems entirely logical that soil solution concentrations of Al should be the determining factors in Al toxicity to plant roots, and that quantities of exchangeable Al serve only to control, in part, such solution concentrations. The data in Tables 9 and 10 support this, in showing the large effects of electrolytes on Al concentrations in equilibrium solutions and on the inhibition of root growth. Though the data are complicated by variable responses to K, the lime-KCl experiment with three soils (Table 9) showed root growth to be far less in soils treated with KCl than in those low in electrolyte. Saturation extracts of the soils after the crop had been harvested contained large concentrations of Al-ions only where KCl, but not lime, had been added.

The experiment involving the factorial combination of $\text{Ca}(\text{OH})_2$ and CaCl_2 applications to acid White Store clay suspension demonstrates the same sort of thing in a more elegant way. Forty per cent neutralization of soil acidity (pH 6) with $\text{Ca}(\text{OH})_2$, which corresponded to around 50 per cent Al-saturation of CECp, resulted in relatively large root development in salt-free systems, where the equilibrium concentration of solution Al was low. The addition of CaCl_2 , however, reduced root growth tremendously (1.9 to 0.2 g), presumably by increasing the solution concentration of Al from <0.05 to 0.8 ppm. The reduction could not have been a salt effect, since the same quantity of CaCl_2 -added to 80 per cent-neutralized clay had little effect on the development of roots.

From the above, it appears that relatively small Al concentrations in soil solutions, less than 1 ppm in some instances, can inhibit the growth of roots of some plant species. The Al concentrations in the equilibrium solutions of soils can logically be regarded as controlled by ion exchange reactions, and to depend on the quantity of exchangeable Al, the percentage Al saturation, the electrolyte concentration, the kinds of other ions in the system, and the appropriate exchange constants. The whole situation is a complex one, and defies quantitative treatment at the present time. However, the general principles which have been developed point to ways in which the problem can be attacked. They provide an adequate qualitative description, and offer the hope that a quantitative one can be obtained.

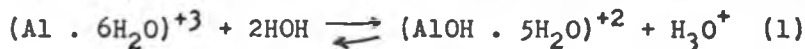
CHARACTERIZATION OF SOILS WITH REGARD TO AVAILABLE ALUMINUM

Relation of pH to Al Concentrations in Soil Solutions

Introduction

The results of the first section of this thesis indicated that Al in the soil solution is primarily responsible for injury to plant roots. To evaluate the tendency of a soil to cause toxicity would then require a knowledge of the "Al-supplying power" of the soil solids to the solution phase. Since acid mineral soils, at least of the southeastern Piedmont and Coastal Plain, contain sizeable quantities of exchangeable Al, any Al-ions going into solution would likely come from exchange sites. Once in solution, part of the Al-ions hydrolyze to form hydroxy-aluminum ions and H-ions; thus the observed acidity of such solutions. The intent in the following work was to relate the pH of soil solutions to their Al concentrations.

When Al salts are dissolved in water, a portion of the Al-ions hydrolyzes, perhaps (Schofield and Taylor, 1954) as indicated by the reaction:



The equilibrium constant is given by:

$$K_h = \frac{[\text{AlOH}^{+2}] \cdot [\text{H}^+]}{[\text{Al}^{+3}]} \quad (2)$$

The brackets denote the activities of the reactant and

product ions. If nothing more basic than AlOH^{+2} is formed, which Schofield and Taylor (1954) found to be the case in the concentration range from 2×10^{-5} to $1 \times 10^{-2}\text{M}$, then,

$$[\text{AlOH}^{+2}] = [\text{H}^{+}] \quad (3)$$

and equation 2 becomes:

$$K_h = \frac{[\text{H}^{+}]^2}{[\text{Al}^{+3}]} \quad (4)$$

Taking the negative logarithms,

$$\text{p}K_h = 2 \text{pH} - \text{pAl} \quad (5)$$

Schofield and Taylor (1954) determined the hydrolysis constant of Al by measuring the pH's of AlCl_3 solutions. Making activity coefficient corrections by means of Debye-Huckel theory, they found $\text{p}K_h$ to be 4.98 at 25°C , with a temperature coefficient of -0.03 units per degree centigrade.

The study described below was based on the hypothesis that soil solutions owe their H-ion concentrations largely to the hydrolysis of Al. If this is the case, the Al concentration in a soil solution could be calculated from equation 5, using a known value for $\text{p}K_h$ and a measured pH. If this is possible, the value of such an interpretation of soil pH would be considerable. The hypothesis was tested by measuring the pH's and Al concentrations of numerous soil solutions, and comparing the measured to calculated Al concentrations.

The $\text{p}K_h$ value of 4.98 (Schofield and Taylor, 1954), is for infinitely dilute solutions. Since no corrections for

ionic strength were made in this study, a more realistic K_h would be an uncorrected one, which would be regarded as a "working" hydrolysis constant applicable to arbitrary but more or less constant experimental conditions. The apparent hydrolysis constant, calculated from Schofield and Taylor's data, over the concentration range of 2×10^{-5} to $1 \times 10^{-3}M$ was 5.19 at $25^\circ C$. Correcting this value to $28^\circ C$, which was more nearly the average temperature encountered in the present work, gave a value of 5.1.

Materials and Methods

A variety of subsoil materials were used in the study to determine the relation of pH to the soil-solution concentrations of Al. The specific soils studied will be described in reporting the results of the experiments.

The usual procedure was to shake 10 g of soil with 50 ml. of a dilute salt solution, most often $0.01M$ $CaCl_2$, for one hour and then to determine the pH and Al concentration of the supernatant liquid obtained by centrifuging. The soil was equilibrated with the salt solutions because Al is held so tightly that without exchanging electrolyte, only minute quantities of Al are found in aqueous extracts. Also, a dilute electrolyte solution was considered more representative of the situation prevailing where fertilizers are added to soils. Calcium chloride was chosen because, with the exception of Al, Ca is the most abundant exchangeable ion in most soils.

The pH readings were taken with a Model H2 or a "Zeromatic" Beckman pH meter. Of the two instruments the "Zeromatic" model seemed superior for giving accurate, reproducible results. The concentrations of Al in the supernatant liquids were determined colorimetrically or by titration. The colorimetric analyses were made using the Eriochrome Cyanine R. method (Jones and Thurman, 1957). Only one modification of the procedure was used; since the soil samples were not treated with Morgan's extractant, 5 ml. of the reagent was added in preparing the samples for color development. The titration procedure for Al involved titrating a sample of the supernatant liquid with NaOH to the phenolphthalein endpoint, adding 2 ml. of neutral 10 per cent KF to a duplicate sample, and titrating it to the same endpoint. The difference between the two titers was taken to equal the base reacting with Al. The measured (experimental) Al concentrations were compared to those calculated by the equation:

$$pAl = 2pH - 5.1 \quad (6)$$

Results

Dependence of soil-solution Al on electrolyte concentration. That the concentration of Al in the solution phase of acid soil-electrolyte mixtures will depend upon the electrolyte concentration is self-evident. The nature of the relationship, however, had to be established by experiments.

To do this, 10 g samples of Creedmoor subsoil, taken from a road bank on U. S. Highway 64 near Pittsboro, North Carolina, were shaken for one hour in 50 ml. of CaCl_2 or KCl solutions of various concentrations. The mixtures were centrifuged, and the Al concentrations in the clear solutions were determined. The Creedmoor soil contained 2.08 meq. exchangeable Al and 0.38 meq. Ca+Mg per 100 g.

Increasing the concentration of the CaCl_2 or KCl increased, by cation exchange, the concentration of Al, and lowered the pH of the solutions (Table 11). The potassium salt was less effective than CaCl_2 in exchanging Al when

Table 11. Effect of salt concentration on the quantity of Al in supernatants from 10 g Creedmoor soil shaken for 1 hour in 50 ml. of salt solutions

Added Salt	Supernatant liquid			
	pH	Al concentration $10^4 \times \text{M}$	pAl	pK _h
1.0 x 10^{-3}M CaCl_2	4.16	0.23	4.63	3.69
3.0 x 10^{-3}M CaCl_2	4.00	0.89	4.09	3.91
6.0 x 10^{-3}M CaCl_2	3.92	1.78	3.75	4.09
1.0 x 10^{-2}M CaCl_2	3.94	2.37	3.62	4.26
2.5 x 10^{-2}M CaCl_2	3.86	4.70	3.33	4.39
5.0 x 10^{-2}M CaCl_2	3.85	6.60	3.18	4.52
2.0 x 10^{-3}M KCl	4.27	0.13	4.88	3.66
6.0 x 10^{-3}M KCl	4.06	0.55	4.26	3.86
1.2 x 10^{-2}M KCl	3.97	1.48	3.83	4.11
2.0 x 10^{-2}M KCl	3.92	2.34	3.63	4.21
5.0 x 10^{-2}M KCl	3.82	5.80	3.24	4.40
1.0 x 10^{-1}M KCl	3.82	7.34	3.13	4.51

the added salt solutions were dilute, but the reverse was noted with more concentrated solutions. The Al concentrations

in Table 11 are also expressed as pAl values, simply for the purpose of orientation, since this method for expressing Al in solution is to be used repeatedly in reporting the results which follow. Values for pK_h , calculated according to equation 5, also are given. They are appreciably smaller than the Schofield and Taylor constant, obtained with homogeneous solutions. The more concentrated the added salt, the greater was pK_h .

Determination of a practical hydrolysis constant. To find out if some practical hydrolysis constant, not necessarily equal to the one reported by Schofield and Taylor (1954), could be found, numerous soil samples were shaken with 0.01M $CaCl_2$, pH's and Al concentrations being determined on supernatant solutions. Calcium chloride was used because of the prevalence of exchangeable Ca in soils; the concentration of 0.01M was chosen for three reasons: 1) In preliminary experiments (Table 11), values for K_h more closely approaching that of Schofield and Taylor (1954) were obtained with relatively concentrated solutions; 2) Schofield and Taylor (1955) have advocated the use of 0.01M $CaCl_2$ to avoid junction potentials and to obtain "lime potentials" ($pH - 1/2 pCa$); and 3) An objective of the present work was to obtain Ca:Al ratios in soil-electrolyte mixtures, and with these and adsorption isotherms, examine relations between such ratios and percentages of Al saturation of soils. Though somewhat more concentrated than ordinary soil

solutions, $0.02N$ was a convenient value for the total concentration of the solutions (C_0) used in determining isotherms.

The first determinations of pH and pAl in $10^{-2}M$ $CaCl_2$ were with Al-saturated samples of Cecil, Appling, White Store and Creedmoor soils. Materials carefully Al-saturated by leaching with $AlCl_3$ were used to avoid the possibility that the exchange of electrostatically bonded H might contribute to the acidity, which could not then be interpreted in terms of the hydrolysis of displaced Al. As shown in Table 12, the pH's ranged from 3.83 to 4.37, the measured pAl's from 3.14 to 4.09, and values calculated for pK_h from 4.52 to 4.65. The average for the latter was 4.60, as

Table 12. Comparison of calculated to measured Al concentrations in the supernatant liquids from 10 g Al-saturated soils, shaken for 1 hour in 50 ml. $0.01M$ $CaCl_2$ (Al determined by titration)

Soil	g soil/flask	pH	Supernatant liquid			
			Exp. pAl	Calc. pAl	ΔpAl	pK_h
Al-Cecil	5	4.15	3.65	3.20	0.45	4.65
Al-Appling	5	4.04	3.46	2.98	0.48	4.64
Al-White Store	2	3.90	3.15	2.70	0.45	4.64
Al-Creedmoor	1	4.37	4.09	3.64	0.45	4.65
Al-Creedmoor	3	4.10	3.68	3.10	0.58	4.52
Al-Creedmoor	5	4.05	3.53	3.00	0.53	4.59
Al-Creedmoor	10	3.94	3.30	2.78	0.52	4.58
Al-Creedmoor	20	3.83	3.14	2.56	0.58	4.52

compared with Schofield and Taylor's (1954) pK_h of 5.10. Also shown in Table 12 are values for pAl calculated from measured pH's and a hydrolysis constant of 5.1, as well as ΔpAl 's, which are differences between measured and calculated values. The measured concentrations of Al were approximately one-third those which would, in $AlCl_3$ solution, correspond to the measured pH's. This implies that Al-ions in soil solution hydrolyze to a greater extent than a similar concentration of ions in pure solution.

Values for pK_h , calculated from the data, were nearly the same for the four soils, and did not change when the quantity of soil was varied twenty-fold. Aluminum ion concentrations approximating closely those measured can be calculated, using the experimental K_h , 4.60.

Next determinations were made using twelve subsoils, all from North Carolina except for the Nason silt loam from near Gordonsville, Virginia. The majority of the subsoils were collected by Mehlich and are shown in Table 13 with the assigned sample numbers. Ten-gram samples of soil and 50 ml. of 0.01M $CaCl_2$ were used. The lowest pH, 3.82, was obtained with the Nason. This soil, with $pAl = 3.32$, also yielded the highest solution concentration of Al (Table 13). At the other extreme was a Cecil sample, with a pH of 5.45 and a pAl of 4.52. Notwithstanding the wide differences among the soils, K_h values, excluding those for the three soils with the highest pH's, ranged from 4.32 to 4.71, and averaged 4.50.

Table 13. Relation of pH to pAl in the supernatant liquid from 10 g subsoil samples shaken for 1 hour in 50 ml. 0.01M CaCl₂ (Al determined by titration)

<u>Subsoil location</u>	<u>Subsoil</u>	<u>pAl</u>	<u>pH</u>	<u>pK_h</u>
Near Gordonsville, Va.	Nason	3.32	3.82	4.32
P 135 S	Georgeville	3.37	3.88	4.39
P 125 S	Wadesboro	3.34	3.92	4.50
P 170 S	Alamance	3.60	3.98	4.36
P 130 S	Herndon	3.46	3.99	4.52
Near Raleigh	Cecil	3.58	4.05	4.52
Near Lenoir	Hayesville	4.06	4.31	4.55
P 149 S	Madison	3.99	4.35	4.71
Near Apex	Granville	4.58	4.57	4.56
P 109 S	Helena	4.52	4.80	5.08 ^a
P 151 S	Lloyd	4.31	5.05	5.79 ^a
P 145 S	Cecil	4.52	5.45	5.38 ^a

^aExcluded from average

Figure 5 shows that the pH-pAl relations obtained for the diverse group of subsoils can be described fairly accurately by a pK_h of 4.5. The three lines in the graph are for hydrolysis constants of 5.1, 4.6 and 4.5, while the points represent data contained in Tables 12 (X's) and 13 (circles).

Another quite similar experiment was conducted with A₂ and B horizons of the Norfolk Catena soils used in the greenhouse experiment described earlier (Table 6). Again, 10 g of soil were shaken with 50 ml. of 0.01M CaCl₂, with pH and Al in solution being measured. Table 14 presents the measured values, and also lists pAl's calculated from

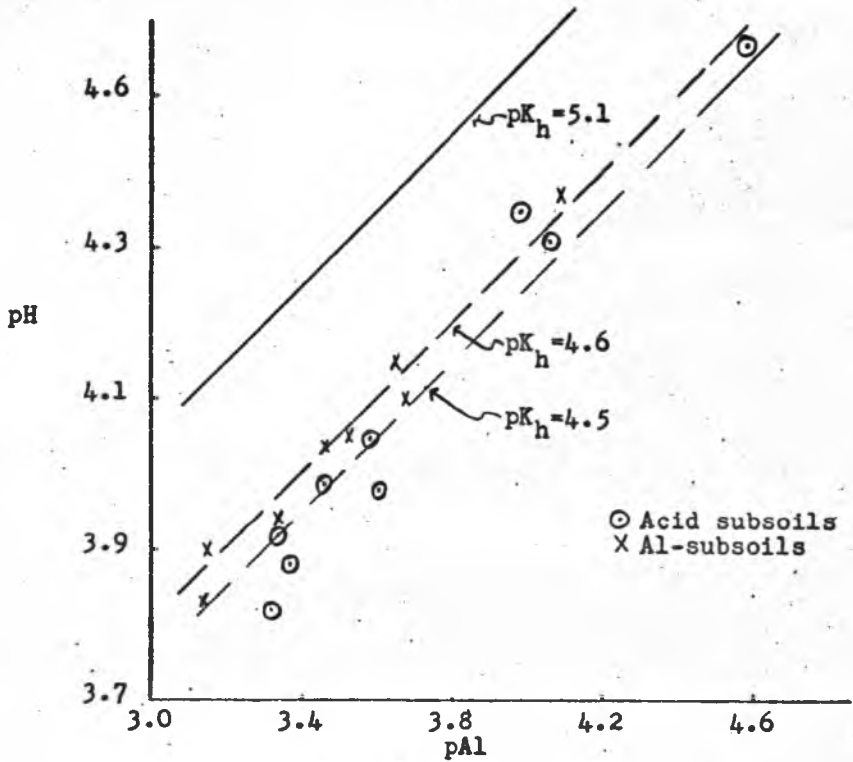


Figure 5. Relation of pH to pAl in the supernatant liquids from 10 g naturally acid and Al-saturated subsoils equilibrated with 50 ml. 0.01M CaCl_2

measured pH's and a pK_h of 5.1. As in the previous experiments, Al concentrations were considerably smaller, or H concentrations were larger, than would be predicted from simple hydrolysis. Surprisingly enough, the deviations generally were largest for the B-horizon samples.

Table 14. Comparison of measured to calculated Al concentrations in supernatant liquids from 10 g Norfolk Catena soils shaken for 1 hour in 50 ml. 0.01M $CaCl_2$ (Al determined colorimetrically)

Soil site	Soils	pH		Exp. pAl		Calc. pAl		ΔpAl	
		A ₂	B ₂	A ₂	B ₂	A ₂	B ₂	A ₂	B ₂
3	Norfolk	4.51	4.10	4.42	4.00	3.92	3.10	0.50	0.90
7	Norfolk	4.47	4.32	4.23	4.45	3.84	3.54	0.39	0.91
2	Goldsboro	4.59	-	4.48	-	4.08	-	0.40	-
9	Goldsboro	4.07	4.10	3.49	3.67	3.04	3.10	0.45	0.57
1	Lynchburg	4.39	4.11	4.02	3.81	3.67	3.12	0.35	0.69
8	Lynchburg	4.53	4.20	4.36	4.15	3.96	3.30	0.40	0.85
4	Rains	4.15	4.02	3.76	3.63	3.20	2.94	0.56	0.69
10	Rains	4.19	4.09	3.59	3.44	3.28	3.08	0.31	0.31
5	Portsmouth	3.91	3.96	3.29	3.13	2.72	2.82	0.57	0.31
6	Portsmouth	4.02	4.13	3.29	3.36	2.94	3.13	0.35	0.23

Practical hydrolysis constants, pK_h , calculated from the data, were somewhat more variable than were those obtained with other sets of soils. Averages, for A₂ and B horizon samples, were 4.69 and 4.50, respectively. Figure 6 shows how the data compare with predictions of "true" and "apparent" hydrolysis constants.

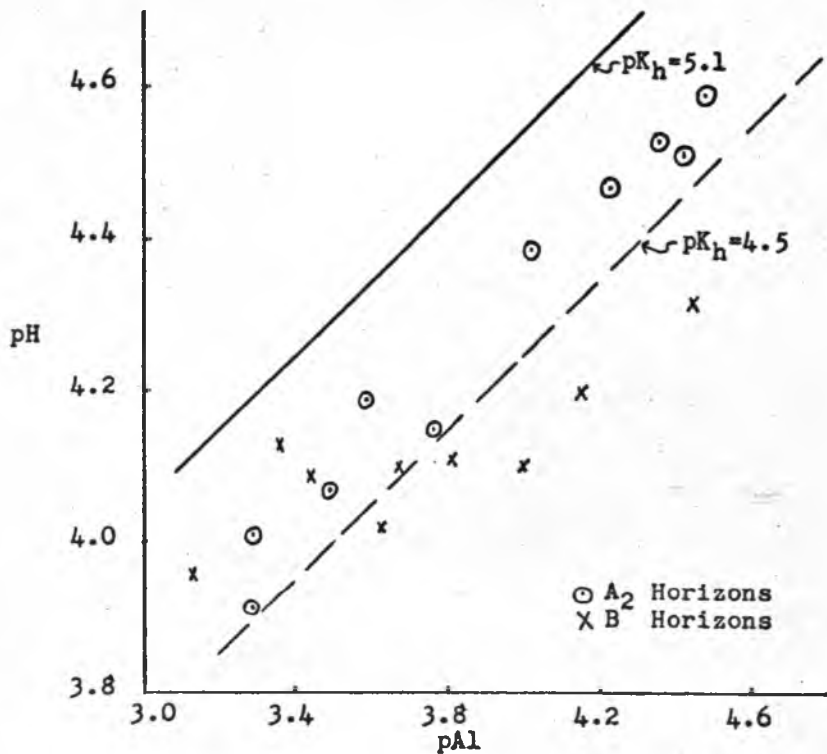


Figure 6. Relation of pH to pAl in the supernatant liquids from 10 g samples Norfolk Catena subsoils equilibrated with 50 ml. 0.01M CaCl_2

Effect of lime on the relation of pH to pAl. All of the work reported to this point was with soils of native ion saturation or Al-soils. Since the largest deviations from theory in the observed pH-pAl relationships were found with nearly neutral materials and because the effect of liming on Al-solubility was of primary interest, an experiment was performed in which the quantity of exchangeable Al equilibrated with 0.01M CaCl_2 solution was varied both by taking different weights of soil and by partially neutralizing some samples with $\text{Ca}(\text{OH})_2$. The treatments were: 1) Equilibrate from 1 to 20 g Al-Creedmoor soil with 50 ml. 0.01M CaCl_2 ; 2) Add sufficient $\text{Ca}(\text{OH})_2$ to achieve 0, 20, 40 and 80 per cent neutralization of the permanent charge acidity of the Al-Creedmoor before equilibrating with the CaCl_2 solutions.

The higher the percentage neutralization was, the closer the experimentally established relationship between pH and pAl approached the theoretical one (Figure 7). Decreasing the concentration of Al by varying the quantity of soil equilibrated with the CaCl_2 did not cause the same result. The data for Figure 7 are presented in Table 15. That $\text{Ca}(\text{OH})_2$ improved the theoretical and measured relationships is seen from the change in pK_h values. They increased from 4.67 to 4.98 with increasing percentage neutralization, but remained fairly constant at about 4.57, where the quantity of Al was varied by using different weights of soil.

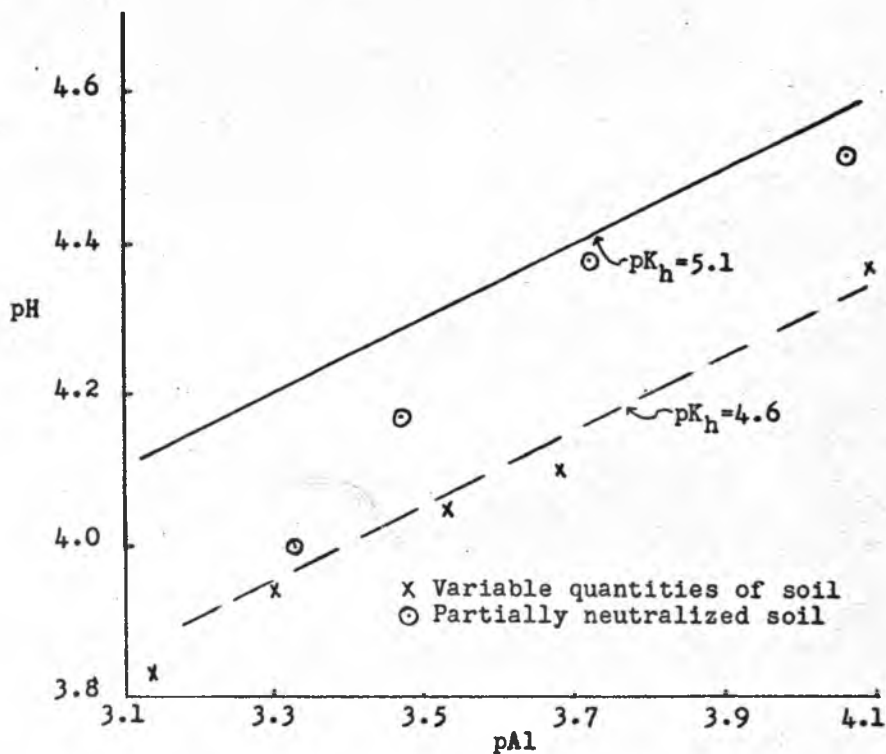


Figure 7. Relation of pH to pAl in the supernatant liquids from 1 to 20 g Al-Creedmoor soil and 10 g partially neutralized Al-Creedmoor soil equilibrated with 50 ml. 0.01M CaCl_2

Table 15. Effect of percentage neutralization and soil to solution ratio on pK_h values for Al-Creedmoor soil (Al determined by titration)

<u>Percentage Neutralization</u>	<u>pH</u>	<u>pAl</u>	<u>pK_h</u>
0	4.00	3.33	4.67
20	4.17	3.47	4.87
40	4.38	3.72	5.04
80	4.52	4.06	4.98
<u>g soil/flask</u>			
1	4.37	4.09	4.65
3	4.10	3.68	4.52
5	4.05	3.53	4.57
10	3.94	3.30	4.58
20	3.83	3.14	4.52

It was reasoned that OH, rather than Ca-ions, were responsible for the increase of pK_h values, since the quantity of Ca added as $Ca(OH)_2$ would be negligible compared to that from the 50 ml. 0.01M $CaCl_2$ solution. Perhaps the added OH-ions altered the system such that fewer H-ions were formed relative to the number of trivalent Al-ions present.

Effect of lime and salt concentration on the relation of pH to pAl. Because liming and fertilizing are treatments common to acid soils, their combined effects on the relation of pH to pAl were investigated. Sufficient $Ca(OH)_2$ was added to 10 g samples of White Store soil (22 meq. exchangeable Al per 100 g) to neutralize 0, 10, 20, 40 or 80 per cent of the exchangeable Al and the mixture shaken overnight.

The suspensions were then made 0.0008 or 0.008M with respect to CaCl_2 , shaken for one hour and centrifuged. The pH and Al concentrations of the supernatants were determined. The Al concentrations were measured colorimetrically.

Just as in the previous experiment, the greater the percentage neutralization, the closer the experimental curve approached the theoretical one (Table 16, Figure 8). The two salt concentrations gave two distinct curves; the one for the more concentrated CaCl_2 solution being considerably closer to the theoretical line. This same result was noted in previous experiments.

Table 16. Effect of salt concentration and percentage neutralization on pH and pAl values for the supernatant liquids from 10 g White Store soil

Percentage neutralization with $\text{Ca}(\text{OH})_2$	pH		pAl	
	CaCl_2 conc. 0.0008M	CaCl_2 conc. 0.008M	CaCl_2 conc. 0.0008M	CaCl_2 conc. 0.008M
0	3.90	3.52	4.41	2.99
10	4.11	3.65	4.64	3.13
20	4.30	3.82	4.78	3.29
40	4.56	4.00	5.10	3.64
80	5.00	4.42	5.34	4.29

The work already reported in this section shows three things:

1. Salt solution-acid soil mixtures yielded solution phases which were acid and which contained

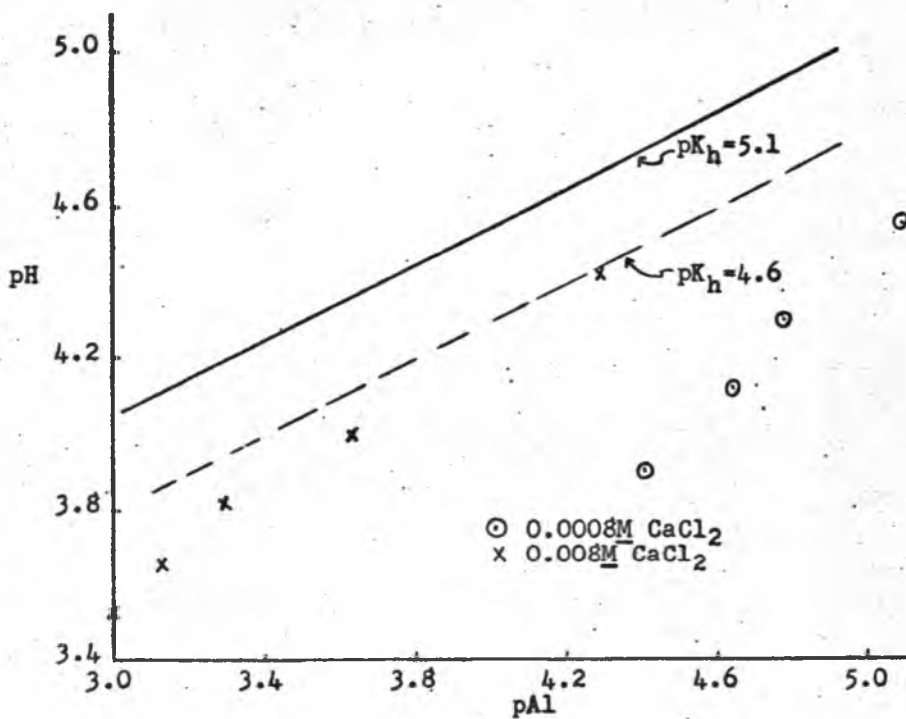


Figure 8. Effect of electrolyte concentration and percentage neutralization on the relation of pH to pAl in the supernatant liquid from 10 g White Store soil equilibrated with 50 ml. 0.0008M or 0.008M CaCl₂

appreciable, and variable, quantities of Al-ions.

2. Relations between Al-concentrations and pH's deviated seriously from those predicted from considerations involving the simple hydrolysis of displaced Al-ions. Aluminum concentrations were invariably too small for measured pH's, or conversely, H-ion concentrations in equilibrium solutions were too large to be accounted for solely through the hydrolysis of Al. Work with Al-saturated soils and clays showed that displacement of exchangeable H did not account for such behavior.
3. At a given electrolyte concentration and for soils other than nearly neutral ones, a practical hydrolysis constant, calculated from measured pH's and pAl's, could be obtained. Such a constant, corresponding to $pK_h = 4.5$ to 4.6 , described the relation between acidity and Al concentration fairly well.

Reasons for low Al concentrations. The reason for Al concentrations in soil-salt solution mixtures being lower than predicted from simple hydrolysis considerations was investigated from several viewpoints. The possibilities of Si solubility and unequal readsorption of hydrolysis products by the soil were considered.

It was imagined that small amounts of silica, solubilized by the added salt, may have been responsible for what seemed

to be too low pH values. With time, the silicic acid, which would form when the Si went into solution, might be expected to be removed from solution by polymerization or sorption on clay surfaces. This would tend to raise the solution pH and, perhaps, cause the measured and calculated pAl values to be equal. The hypothesis was investigated by equilibrating Creedmoor soil samples with salt solutions for one hour or for eight days. A series of CaCl_2 and KCl concentrations were used in order to get a range of Al concentrations in solution.

The pH of the supernatant liquids increased with time (Table 17), but the concentration of Al decreased, so that the theoretical and measured relationship between pH and pAl was not greatly improved (Figure 9). This was unexpected, and was studied in work to be reported in a following section of the thesis. The percentage decrease in Al concentrations with the soil-KCl mixtures was generally less than with the CaCl_2 solutions. With the highest KCl concentration used, 0.1M, there even appeared to be an increase in the concentration of Al in the supernatant with time (Table 17).

The slopes of the lines drawn through the experimental points in Figure 9 deviate considerably from those of the theoretical lines. This is another manifestation of the effect of electrolyte concentration on the apparent exchange and hydrolysis equilibria. Large pH and pAl values in the Figure correspond to dilute solutions. As shown before,

the largest departures from theory occur when only a little Al is exchanged into solution.

Table 17. Effect of shaking time on the relation of pH to pAl in the supernatant liquids from 10 g Creedmoor soil shaken in 50 ml. CaCl₂ or KCl solution

Added salt	Supernatant liquid			
	pH		Al conc. ($10^4 \times M$ Al)	
	1 hr. shaking	8 days shaking	1 hr. shaking	8 days shaking
1.0 x 10 ⁻³ M CaCl ₂	4.16	4.45	0.23	0.13
3.0 x 10 ⁻³ M CaCl ₂	4.00	4.23	0.89	0.53
6.0 x 10 ⁻³ M CaCl ₂	3.92	4.18	1.78	0.67
1.0 x 10 ⁻² M CaCl ₂	3.94	4.14	2.37	1.03
2.5 x 10 ⁻² M CaCl ₂	3.86	4.10	4.70	2.87
5.0 x 10 ⁻² M CaCl ₂	3.85	4.10	6.60	3.74
2.0 x 10 ⁻³ M KCl	4.27	4.65	0.13	0.04
6.0 x 10 ⁻³ M KCl	4.06	4.30	0.55	0.26
1.2 x 10 ⁻² M KCl	3.97	4.18	1.48	0.92
2.0 x 10 ⁻² M KCl	3.92	4.12	2.34	1.53
5.0 x 10 ⁻² M KCl	3.82	4.00	5.80	4.70
1.0 x 10 ⁻¹ M KCl	3.82	3.97	7.34	8.61

A second, and more tenable, hypothesis concerning the reason for the general finding that pH's in salt extracts of soils were too low to have been caused solely by the hydrolysis of Al was that hydrolysis products, H⁺ and AlOH⁺⁺, may be sorbed unequally by the soils, thus shifting equilibrium and building up the concentration of the more weakly sorbed product.

To investigate this, the Al-saturated soils from preceding work and a Portsmouth B horizon soil (Table 1, site 5) were used. Since the pH's always seemed too low,

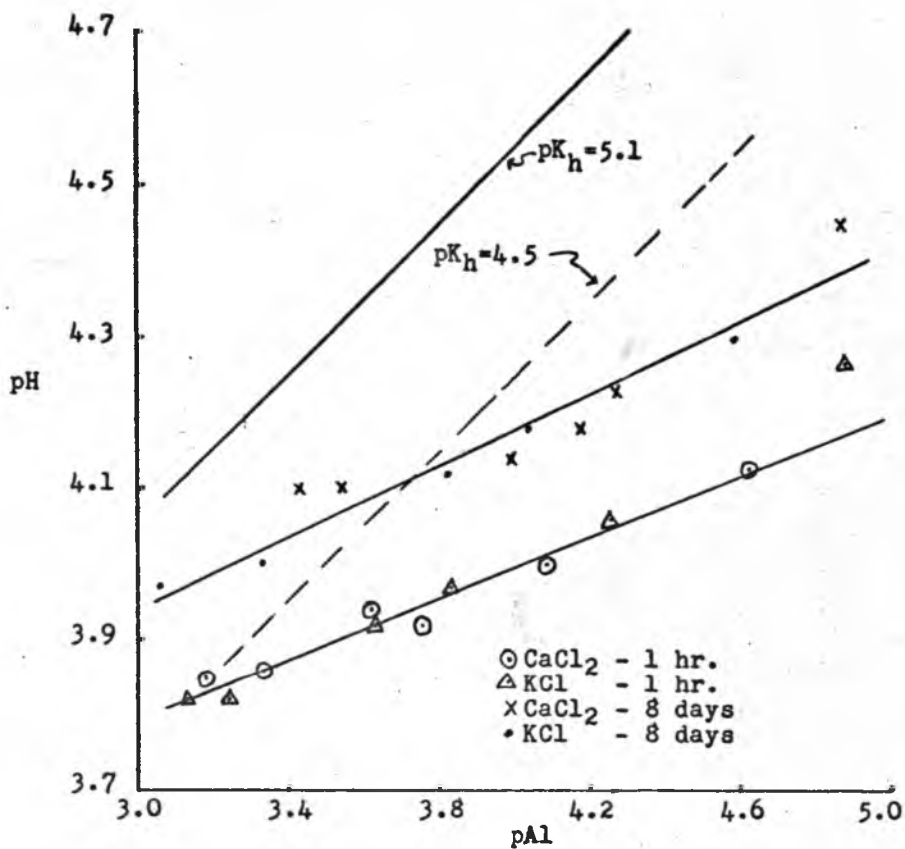


Figure 9. Effect of shaking time on the relation of pH to pAl in the supernatant liquids from 10 g Creedmoor soil equilibrated with 50 ml. CaCl₂ or KCl solution

it was expected that if unequal sorption occurred, the AlOH^{+2} -ions would be preferred. If there were a tendency for more of the AlOH^{+2} than H-ions to be sorbed by the clay, then a disproportionate part of the H-ions in the system would remain in the supernatant liquid upon centrifugation. The procedure used for determining the excess of H- over AlOH^{+2} -ions was to titrate two aliquots of the supernatant liquid with sodium hydroxide, sufficient KF being added to one aliquot to complex all the Al^{+3} and AlOH^{+2} before titrating. The quantity of H-ions left unneutralized where KF was added was taken to equal the extent to which preferred AlOH^{+2} re-sorption had occurred. This seems valid, since the OH-ions replaced from the AlOH^{+2} by the F-ions would neutralize H-ions in amount of AlOH^{+2} -ions present. The quantity of soil and the CaCl_2 concentration was varied to get a range of Al concentrations and perhaps a difference in the preferred re-sorption of AlOH^{+2} -ions.

The more concentrated the CaCl_2 solution, or the wider the soil-salt solution ratio, the smaller was the percentage preferred re-sorption (Table 18). This is a reasonable result since in these situations a greater proportion of the CECp of the soil would have been Ca-saturated. It was interesting to note that preferred re-sorption seemed no greater with the Portsmouth soil than with the Al-saturated soils. This may support the contention that there is very little electrostatically bound H in soils.

Table 18. Preferred re-sorption of $AlOH^{+2}$ -ions by 10 g soils shaken for 1 hour in 50 ml. of $CaCl_2$ solutions

Soil	g soil/flask	$CaCl_2$ conc. M	pH	% Preferred re-sorption
Al-Creedmoor	10	1.00	3.85	0
Al-Creedmoor	10	0.10	4.00	4
Al-Creedmoor	5	0.10	4.10	10
Al-Creedmoor	2	0.10	4.28	24
Al-Creedmoor	10	0.01	4.00	18
Al-Cecil	5	0.01	4.15	18
Al-Applying	5	0.01	4.04	15
Al-White Store	2	0.01	3.90	14
Portsmouth	10	0.01	3.98	17

The extent of preferred re-sorption was about 18 per cent when the salt solution concentration was 0.01M. To correct the measured Al concentrations by this amount does not, however, bring the experimental and calculated pAl values much closer together. The conclusion is drawn that preferred re-sorption probably occurs, but it is not large enough to account for the differences between experimental and calculated Al values.

Though Schofield and Taylor (1954) state that nothing more basic than $AlOH^{+2}$ forms in the concentration range covering these experiments, perhaps a system containing soil causes greater hydrolysis than would occur in pure solutions. If $Al(OH)_2^+$ were formed, then greater than one H-ion would be

formed per Al-ion which hydrolyzed. This would cause the pH to be too low for the theorized relationship to hold.

Discussion

The hypothesis that the pH of acid soil-salt solution mixtures was due largely to H-ions produced by hydrolysis of Al-ions in solution was investigated. Aluminum concentrations in the supernatant liquids from these mixtures were calculated from the relationship

$$pAl = 2 pH - 5.1 \quad (6)$$

and compared with the experimental values. Invariably the measured Al concentrations were smaller than the calculated ones, indicating that the observed pH's were too low for all of the H-ions to have come from the simple hydrolysis of Al. This is providing that nothing more basic than $AlOH^{+2}$ was produced in the hydrolysis reaction. Neither saturation of the soils with Al, nor correction for preferred re-sorption of $AlOH^{+2}$ over H-ions, improved the agreement between measured and calculated Al concentrations very much.

Since there was a definite relationship between pH and pAl, though not precisely the one predicted by the first hydrolysis constant of Al, it is proposed that an experimental or practical hydrolysis constant be determined. Such a constant may be calculated for a group of soils, and could possibly be used to predict from pH measurements, the concentrations of Al to be expected in soil solutions.

The practical hydrolysis constant for a group of Al-saturated soils and a number of naturally acid subsoils was found to be 4.50 ± 0.3 . Large variations were observed with partially neutralized Al-soils or soils with natural ion saturations corresponding to pH 5.0 or greater. The higher the percentage base saturation, the larger was the "practical" hydrolysis constant.

The question of what happens to Al-ions displaced by neutral salts was not resolved in the preceding section, and will be considered in more detail later. It is clear, however, that some re-sorption of hydrolysis products must take place, so that ion exchange equilibria involving Al are complicated not only by hydrolysis, but by subsequent reactions as well.

Although specific comparisons were not made, the concentrations of Al in the supernatants from 10 g soil in 50 ml. 0.01M CaCl_2 were in the order of magnitude of those found in saturation extracts from unlimed soils. Measured pAl's varied from around 3 to 4, corresponding to Al concentrations between 0.3 and 3 m moles per liter, or 8.1 to 81 ppm Al. In order to use a procedure such as the one described in the foregoing section, for a group of soils, the concentration of the salt solution which is added to the soil would have to be adjusted to yield Al concentrations similar to those in soil solution extracts of the soils. Since the Al concentration in soil solution extracts is directly dependent on

electrolyte concentration, the kind and amount of added fertilizer would have to be considered also.

Ion Exchange Equilibria Involving Ca and Al

Introduction

In attempting to generalize relations between the quantities of exchangeable Al present in soils and Al concentrations in soil solutions, it is essential that information on appropriate ion exchange equilibria be available. Other than that Al-ions appear to be adsorbed strongly, little is known about the ways in which they participate in exchange reactions. Much of the material which has been presented in earlier sections has indicated that ion exchange, involving the displacement of Al, is complicated by hydrolysis and re-sorption of hydrolysis products. From this, it might appear useless to attempt the study of exchange equilibria involving Al. Under appropriate experimental conditions, however, it seems possible to measure quantities of Al and of some other cation on exchange sites, and the corresponding equilibrium solution concentrations. The next section deals with the results of such experiments.

Although the idea seems prevalent among soil scientists that equilibrium constants, which describe ion exchange involving a given pair of ions and a given adsorbent, can be obtained (Krishnamoorthy and Overstreet, 1949), this does not seem to be generally true (Gaines and Thomas, 1955).

Instead, it seems preferable to study ion exchange over the widest possible range of equivalent fractions on

exchange sites of the ions concerned, and to describe the results not in terms of exchange constants but in terms of adsorption isotherms.

Materials and Methods

Experiments to obtain such information were conducted first with Utah bentonite and White Store B₂ as the adsorbents and then with Norfolk and Portsmouth A₂ and B horizon materials. The specific properties of the adsorbents and the procedures used are described with the results of these experiments.

Results

Utah bentonite and White Store B₂. A series of solutions of total concentration (C_0) 0.01N were prepared by mixing $AlCl_3$ and $CaCl_2$ solutions. Equivalent fractions of Al (c/c_0) were varied stepwise from 0.03 to 0.98. Since it was anticipated that small amounts of Ca would be adsorbed from solutions where the major proportion of the solution was made up of Al-ions, all solutions with c/c_0 greater than 0.5 were spiked with carrier-free $Ca^{45}Cl_2$, to aid in analysis for equilibrium quantities of exchangeable Ca.

One-gram samples of Utah bentonite or two-gram samples of White Store (1-40 mm mean aggregates, stabilized with 0.1 per cent VAMA), (CECp = 0.84 and 0.22 meq. per g,

respectively) were leached with $1N$ $CaCl_2$ to achieve Ca-saturation and then were washed with distilled water to remove excess Cl. Then 500 ml. portions of the various $AlCl_3$ - $CaCl_2$ saturating solutions were leached slowly through duplicate samples of Ca-clay or soil. That the resulting ion populations of the exchange sites were in equilibrium with the leaching solutions was verified by passing 500 ml. more of solutions of high or low c/c_0 through certain samples, with no changes in the quantities of the exchangeable ions.

After the leaching treatment, the clay or soil samples were washed with 75 per cent ethyl alcohol until free of Cl, and then were leached with 100 ml. $1N$ KCl to displace the exchangeable Ca and Al. Aluminum in the leachates was measured by titration with standard NaOH. For leachates from samples where c/c_0 was smaller than 0.5, Ca was determined by titration with Na_2EDTA , after the removal of Al by precipitating at pH 8 and centrifuging. Where c/c_0 was larger than 0.5, Ca^{45} tracer was used for the Ca analysis. Sufficient carrier Ca was added to the KCl leachates to give approximately constant total Ca concentration and, furthermore, to give infinitely thick samples upon the precipitation of calcium oxalate and mounting for the assay of radioactivity. Calcium (carrier + Ca^{45} -labeled Ca displaced from the clay or soil) was precipitated with ammonium oxalate at pH 6. The precipitates were collected on circles of glass filter paper

and, after washing and drying with ethyl alcohol and acetone, were counted with a gas flow geiger tube with a micromil window.

Standards containing known amounts of Ca^{45} (known in terms of the spikes added to the leaching solutions) and the same quantities of carrier Ca as the leachates were carried through the same procedure. The percentage of the Ca in each leaching solution which was held up by the soil or clay could thus be calculated, and from this and the Ca concentration, the quantities of sorbed Ca corresponding to each value of c/c_0 were determined.

Duplication in quantities of Ca and Al adsorbed from particular leaching solutions was within 5 per cent. For all of the values of c/c_0 , the sum of Ca and Al adsorbed was constant to within 5 per cent, and was very close to CECp for each sorbent.

The results of the above work, which involved measurements at thirteen different values of c/c_0 for the Utah bentonite, and at ten for the White Store, are presented in Figure 10, which is a graph of q/q_0 , the proportion of the CECp countered by Al, against c/c_0 , the proportion of the total solution concentration made up of Al. Two points illustrated by Figure 10 are of particular interest. First, from 0.01N solutions, Al is greatly preferred over Ca. In fact, the Al-saturation was greater than 90 per cent soon after c/c_0 was 0.5 and continued to increase thereafter.

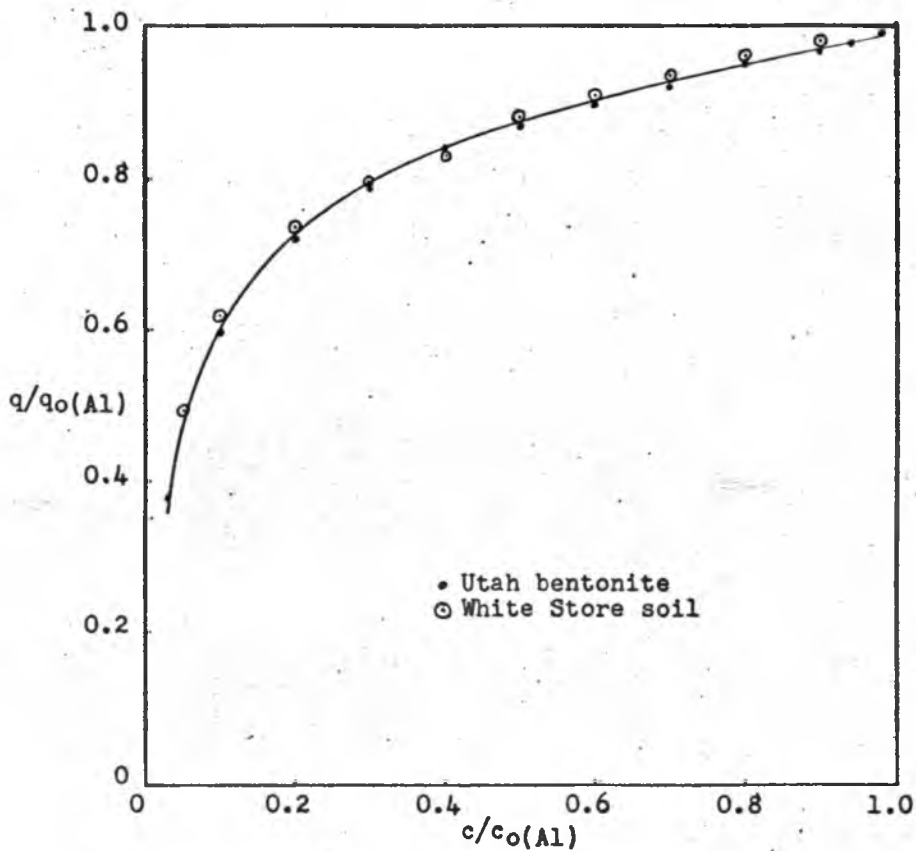


Figure 10. Al-Ca adsorption isotherm for Utah bentonite and White Store soil ($c_0 = 0.01\text{N}$)

Of equal interest is the fact that the isotherms for the two sorbents, one soil and the other montmorillonite, were almost superimposed. This indicates a greater importance of the cations than the type of adsorbent in controlling exchange equilibria.

One can calculate apparent exchange constants for the various points in Figure 10 by the relation:

$$K'_c = \frac{[q/q_0]^2 \cdot [1-c/c_0]^3}{[1-q/q_0]^3 \cdot [c/c_0]^2} \cdot C_0 \quad (7)$$

The values for K'_c listed in Table 19 were calculated from the smooth curve in Figure 10, and are representative both for Utah bentonite and White Store. As often appears to be the case in exchanges between dissimilar ions, Al was

Table 19. Apparent exchange constants for Al-Ca exchange, $C_0 = 0.01N$. Calculated with points from adsorption isotherm for Utah bentonite and White Store soil

$c/c_0(Al)$	$q/q_0(Al)$	K'_c
0.05	0.470	5.09
0.10	0.600	4.11
0.20	0.720	3.02
0.30	0.800	3.05
0.40	0.840	2.32
0.50	0.870	1.72
0.60	0.900	1.60
0.70	0.930	1.39
0.80	0.950	0.90
0.90	0.975	0.75

more strongly preferred at high Ca saturations; Ca was bound

somewhat more tightly for large values of c/c_0 . Over the range of c/c_0 from 0.05 to 0.90, the apparent exchange constant varied by a factor of about 6.8.

Norfolk and Portsmouth soils. Because these soils have low exchange capacities relative to the adsorbents just discussed, the procedure for studying exchange equilibria with these materials had to be changed considerably. Instead of removing and measuring the adsorbed ions, the proportions of the CECp countered by Al and Ca were determined by leaching columns of the soil with Al-Ca solutions until equilibrium was established, then passing an Al-Ca⁴⁵ solution of known concentration through the soil and determining the Ca⁴⁵ in the leachate. Knowing the difference between the meq. Ca in the leaching solution and that in the leachate and the CECp of the soil sample, the proportion of the exchange capacity Ca-saturated could be calculated. This procedure avoids the necessity for counting vanishingly small quantities of Ca⁴⁵ and the uncertainties which arise from displacing excess electrolyte.

Soil material from the Norfolk A₂ and B horizons (Table 5, site 7) and the Portsmouth A₂ and B horizons (Table 5, site 5) was used in this study. One to five-gram samples were leached with 1N then 0.001N CaCl₂ solutions to achieve homoionic saturation. The Ca-saturated soil samples were then leached with mixtures of AlCl₃ and CaCl₂, whose total concentration (C₀) was 0.001N, until equilibrium or

near-equilibrium was established. The less concentrated solution, $0.001N$, was used, for it would be closer to the total concentration of ions in naturally occurring soil solutions. Three solutions containing 0.2, 0.5 and 0.8 equivalent fractions (c/c_0) were used. When equilibrium was reached between the exchange sites and the leaching solutions was determined by taking aliquots of the leachate and colorimetrically comparing their Al concentrations with the leaching solutions. When the two were equal, equilibrium was assumed to be established.

After this the soil samples were leached slowly with the 200 ml. of the same Al-Ca solutions, to which had been added a spike of carrier-free Ca^{45} . Sufficient carrier Ca was added to the leachate to give, on precipitation and filtration, infinitely thick samples for counting. The Ca was precipitated with ammonium oxalate at pH 6 and collected on discs of glass filter paper. After washing and drying with ethyl alcohol and acetone the precipitates were counted with a gas flow geiger tube with a micromil window. These counts were compared with counts for standards which were prepared and counted in the same manner. The percentage of the Ca^{45} held up times the meq. Ca in the 200 ml. of leaching solution divided by the CECp of the soil sample was taken to equal the proportion of the CEC Ca-saturated. The remainder of the CECp was assumed to be Al-saturated. Amphlett and McDonald (1956) have used a similar single-tracer technique.

The procedure followed in determining the CECp of the four soil materials was to Ca-saturate a soil sample, then leach with $1N$ $AlCl_3$, wash with H_2O until free of Cl , displace the adsorbed Al with $1N$ $NaCl$ and measure the Al in the $NaCl$ leachate (Jones and Thurman, 1957).

A prerequisite for any ion exchange study is that exchange equilibria be established before the proportions of the two ions saturating the adsorbent are determined. This was never obtained in this study where .0.2 of the cations in the leaching solution were Al (Table 20). When the solutions were either 0.5 or 0.8 Al , the concentrations of Al in the leachate became equal to those of the leaching solutions after a few symmetries of the cations had been passed through the soil sample. It was decided, because of what seemed an endless consumption of Al -ions from the 0.2 Al solution ($0.0008N$ Ca + $0.0002N$ Al), that Al must be precipitating somewhere in the system as $Al(OH)_3$. This idea is perhaps supported by considering the pH of the leaching solutions, which are shown below:

Leaching solution pH values

$c/c_0(Al)$	Leaching solutions		
	N Al	N Ca	pH
0.2	0.0002	0.0008	4.65
0.5	0.0005	0.0005	4.50
0.8	0.0008	0.0002	4.38

The solution with the least proportion of Al had a pH of 4.65;

the one with most Al, a pH of 4.38. Though it would not occur in pure solutions, perhaps a pH of 4.65 is sufficiently

Table 20. Comparison of Al concentrations in 0.2 Al leaching solutions and in leachates from Norfolk and Portsmouth soils

<u>Sample</u>	<u>Symmetries Al through soil</u>	<u>O.D.</u>
0.2 Al leaching solution		<u>0.260</u>
Norfolk A ₂ leachate	0.22	0.143
" " "	0.58	0.156
" " "	0.83	0.206
" " "	1.67	0.220
Norfolk B ₂ leachate	11.10	0.165
" " "	12.90	0.207
" " "	16.60	0.207
Portsmouth A ₂ leachate	3.02	0.200
" " "	4.15	0.220
" " "	6.79	0.220
" " "	7.55	0.230
" " "	9.43	0.220
Portsmouth B leachate	0.95	0.116
" " "	1.90	0.122
" " "	2.86	0.178

high to cause precipitation of Al when the AlCl₃ solution is in contact with soil material. It is not known if such a precipitation reaction would change the proportion of CEC_p saturated with the two ions. The values obtained where it occurred, $c/c_0 = 0.2$, indicate that it would not.

The proportions of the CEC_p of the four soil materials Al-saturated by exchange with the three leaching solutions are shown in Figure 11. Also shown, as a frame of reference,

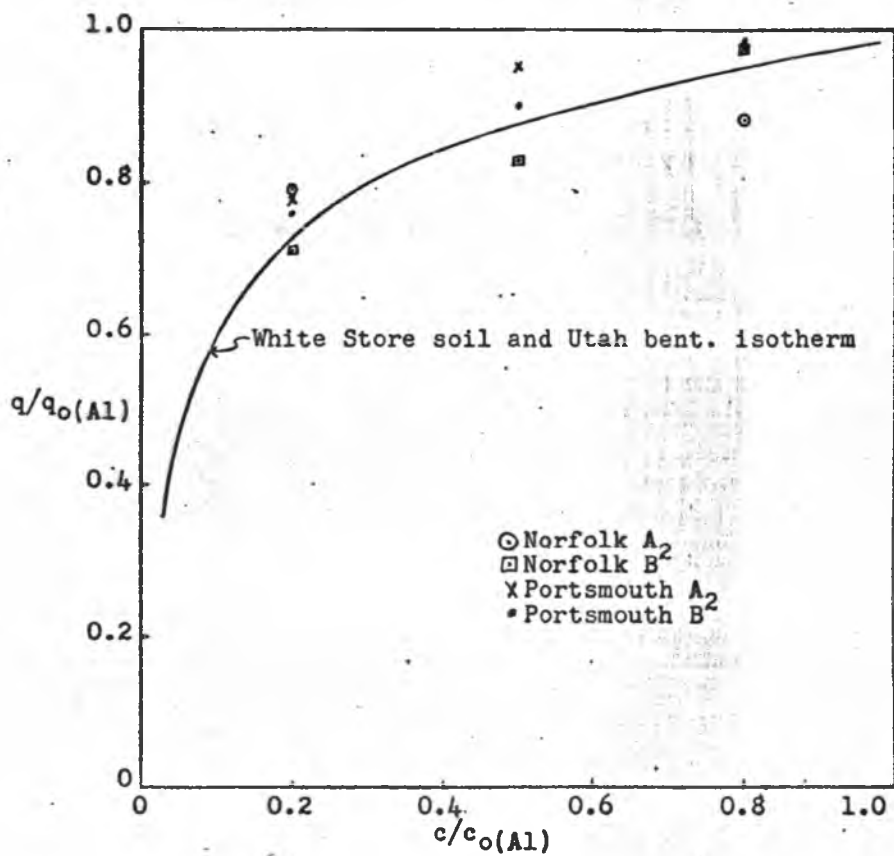


Figure 11. Adsorption of Al on Ca-saturated Norfolk Catena soils ($c_0 = 0.001N$)

is the adsorption isotherm, determined in the previous study, for Utah bentonite and White Store soil. As was the case with the high-exchange capacity materials, Al was strongly preferred over Ca. With three exceptions, the points were above the curve for the Utah bentonite and White Store soil. This is the expected result with a lower C_0 . The Norfolk A₂ deviated seriously from the other soil by showing a much higher apparent affinity for Ca at high c/c_0 values. Whether this point is in error or is representative of a true difference in behavior is not known.

Discussion

An attractive prospect presents itself for determining percentages of Al-saturation by a simple pH measurement when the adsorption isotherm and the "practical" hydrolysis constant for a group of soils is known. That such is the possibility is indicated by considering some of the data already presented. Since no experiments were performed with this specific purpose in mind, data from several experiments must be used. The only well-established adsorption isotherm available was obtained with Utah bentonite and White Store B₂ ($C_0 = 0.01N$), and the only pH and "practical" hydrolysis constants determined for soils with known percentages Al-saturation are for Norfolk Catena soils equilibrated in $0.02N$ $CaCl_2$. The procedure followed was to use the average hydrolysis constants for Norfolk Catena A₂ and B horizon soils,

which were 4.67 and 4.49 respectively, and the pH's of Norfolk Catena soil - 0.02N CaCl_2 mixtures (Table 14) to calculate solution concentrations of Al. These concentrations were divided by 0.02N to give $c/c_{o(\text{Al})}$ values, which were then used to go into the adsorption isotherm (Figures 10 or 11) and read the corresponding Al-saturations of the adsorbent.

The percentages of Al saturation of several Norfolk Catena soils determined by leaching the soils with 1N NaCl (Table 5) are listed in Table 21. Also shown are the

Table 21. Comparison of measured to calculated percentages Al-saturations of Norfolk Catena soils

Soil site	Subsoil	Measured percentage Al sat.	Calculated percentage Al sat. ^a	$c/c_{o(\text{Al})}^a$
4	Rains A ₂	47	40	0.035
10	Rains A ₂	59	35	0.030
5	Portsmouth A ₂	71	61	0.106
6	Portsmouth A ₂	80	53	0.064
3	Norfolk B ₂	31	35	0.030
7	Norfolk B ₂	22	19	0.011
1	Lynchburg B ₂	51	33	0.028
8	Lynchburg B ₂	32	16	0.018
4	Rains B _g	59	46	0.042
10	Rains B _g	63	37	0.031
5	Portsmouth B _g	74	51	0.056
6	Portsmouth B _g	67	32	0.026

^aTaken from adsorption isotherm, using c/c_o values calculated from pH measurement of soil-0.01N CaCl_2 mixtures and an average pK_h of 4.67 for A₂ horizon soils and 4.49 for B horizon soils.

percentages of Al saturation determined in the manner just described. The agreement between the two is far from perfect, but perhaps close enough to indicate possible usefulness. The fact that $c/c_{o(Al)}$ values were all less than 0.1 brings out the need for adsorption isotherms to be thoroughly characterized in the trace region. The isotherm used in this case was least well-characterized in this region.

Accelerated Hydrolysis

Introduction

A common observation in the experiments to characterize the "available" Al in soils, was the tendency of Al to "disappear" from soil-solutions with time. Several experiments designed to find the cause and extent of the solution-to-solid phase reaction were performed. Both continuously wet systems and those subjected to wetting and drying treatments were studied.

Materials and Methods

The Creedmoor, White Store and Cecil soils and Utah bentonite were used in these studies. The specific properties of these materials are described with the results of the experiments. The procedure followed in studying the continuously wet systems was to shake acid soil-salt solution mixtures from thirty minutes to several days and note the change in the concentration of Al in the solutions with time. In some instances changes in quantities of exchangeable Al were also measured.

In the experiments where the soil samples were wet and dried, the acid soil or clay samples were mixed with a salt solution, placed in an 80°C oven to hasten the reactions, and any changes with time of solution phase Al, Ca and Cl measured. The exchangeable cations were measured also.

Results

Continuously wet systems. The conversion of soil-solution Al to insoluble Al, in stoppered soil-salt solution mixtures, was first noted in the experiment reported in Table 17. Within a period of eight days, as much as 50 per cent of the solution Al had "disappeared".

First, a series of flasks containing 10 g Creedmoor soil (CECp = 2.46 meq., with 2.08 meq. exchangeable Al/100 g) and 50 ml. 0.01M CaCl_2 were shaken from thirty minutes to sixty days. Flasks were removed from the shaker periodically, the mixtures centrifuged, and the supernatants analyzed for Al (Jones and Thurman, 1957). Over the two-month period, the solution concentration of Al in the soil-salt solution mixtures decreased from 2.88 to $0.33 \times 10^{-4}\text{M}$ (Table 22). The Al concentration decreased steadily through the fifteenth day and then increased until the forty-second day, after which it decreased again. The only treatment difference during the period of apparent increase was non-continuous shaking of the mixtures. Why such an effect should result is not apparent.

Though the Creedmoor is not a soil which characteristically adsorbs chloride (Berg and Thomas, 1959), this was considered a possible explanation for the "disappearance" of Al. Aliquots of the supernatant liquids were analyzed

for Cl (AgNO_3 titration) to determine if adsorption had occurred (Table 22). The data indicate that no Cl-adsorption occurred, but since the concentration of Cl was about one-hundred-fold greater than that of the Al, a small but sufficient adsorption of Cl may have occurred without being detected.

Table 22. Effect of time on the concentration of Al in the supernatant liquid from 10 g natural Creedmoor soil in 50 ml. 10^{-2}M CaCl_2

<u>Shaking time</u>	<u>Al Conc.</u> (10^4xM)	<u>Cl Conc.^a</u> (10^2xM)
30 min.	2.88	2.12
1 day	2.63	2.14
4 days	2.50	2.14
8 days	2.07	2.10
15 days	1.28	2.12
33 days	1.38	2.13
36 days	1.48	2.10
42 days	1.55	2.08
60 days	0.33	2.08

^aCl concentration of added CaCl_2 solution: $10^2 \times 2.15\text{M}$

If Cl-adsorption were responsible for the observed "disappearance" of soil-solution Al, then any Al removed from solution would be held in an exchangeable form. The previous experiment was repeated with Al-saturated Creedmoor soil, and this time exchangeable, as well as soil-solution, Al was measured. In twenty-eight days, the concentration of Al in the supernatant liquids had decreased from 4.15 to $1.78 \times 10^{-4}\text{M}$, and the exchangeable Al changed from 1.28 to

0.66 meq. per 100 g soil (Table 23). These results discount strongly the idea of Cl-adsorption, but again indicate the dependence of solution Al on a reservoir of exchangeable Al.

Table 23. Effect of time on solution pH and Al and the exchangeable Al of 10 g Al-Creedmoor soil in 50 ml. 0.01M CaCl_2

<u>Shaking time</u>	<u>Supernatant liquid</u>		<u>Exch. Al meq./100g</u>
	<u>pH</u>	<u>($10^{-4}M$) Al</u>	
30 min.	3.62	4.15	1.28
7 days	3.98	2.97	1.24
14 days	4.06	2.52	1.05
21 days	-	1.95	0.86
28 days	-	1.78	0.66

Other possible reasons for the decrease of soil-solution Al were considered: 1) An increase in pH due to the release of basic ions from weatherable soil minerals or the glass containers and; 2) Reaction of Al with Si released from dissolving minerals or glass. There was a substantial increase in the pH of supernatants from the Al-Creedmoor samples with time. Within two weeks the pH increased from 3.62 to 4.06 (Table 23). Whether this increase was due to basic ions coming into solution, or was the result of Al-ions going out of solution, cannot be established from this experiment.

That glass solubility was not responsible for the observed "disappearance" of Al is shown by comparing the changes in solution Al with time for Al-Creedmoor- CaCl_2 mixtures shaken in glass versus polyethylene containers (Figure 12). Although the rate of Al "disappearance" was a little greater for samples shaken in glass, this is not considered significant, because the time periods over which the samples were shaken was not the same. A small difference in the average room temperature may have caused the observed difference.

To investigate the possibility of basic ions, released from dissolving soil minerals, being responsible for the loss of solution Al, the following procedure was used; ten-gram samples of Al-Creedmoor soil were mixed with 50 ml. 10^{-4}M AlCl_3 , were shaken for thirty minutes to thirty-five days, samples were centrifuged periodically and the clear solution analyzed for Al colorimetrically. There was a rapid initial drop in solution Al and after that a slower "loss" such that by the thirty-fifth day only 14 per cent of the solution Al initially present remained (Table 24).

Since the soil samples were Al-saturated and were shaken in solutions of AlCl_3 , it would seem that any ions responsible for the precipitation of Al must have come from the decomposition of soil minerals. Perhaps this argument is substantiated by the fact that the most rapid Al "disappearance" was in the first week of shaking where the

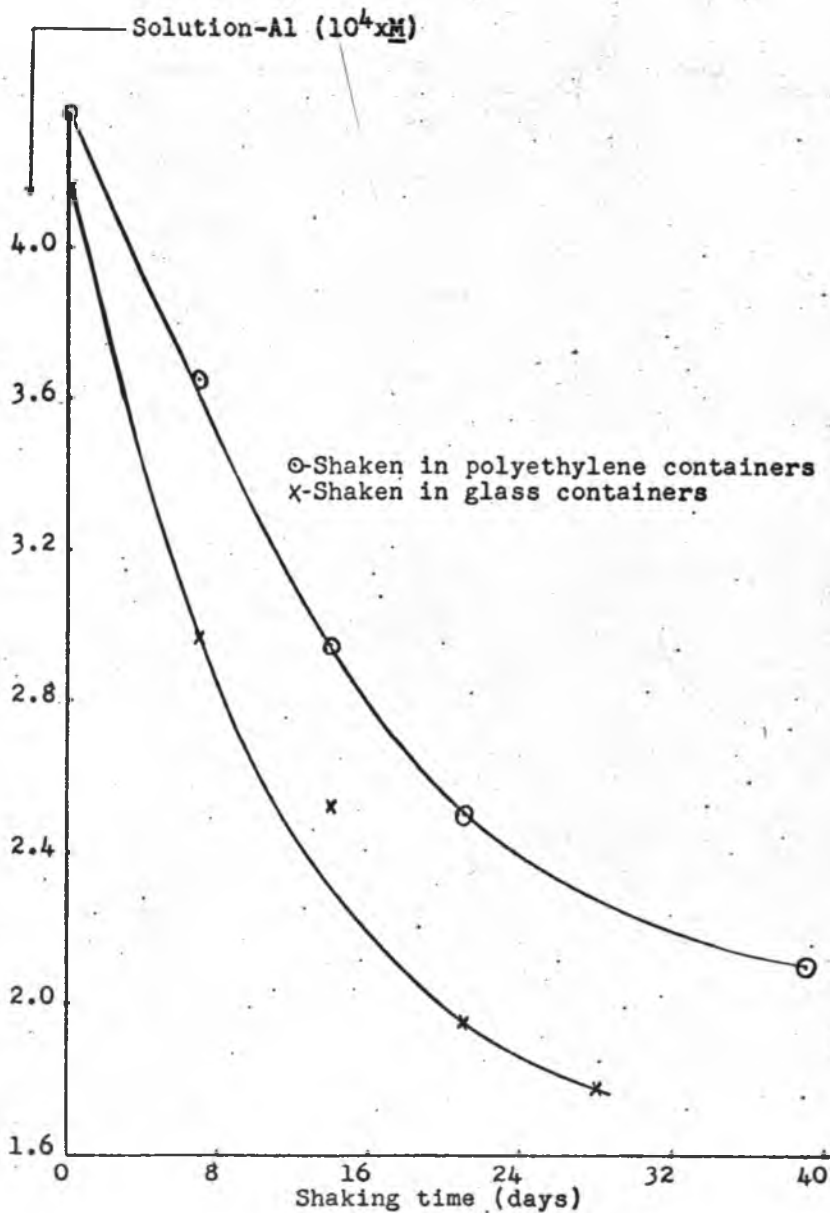


Figure 12. "Disappearance" of solution-Al with time from 10 g Al-Creedmoor soil equilibrated with 50 ml. 0.01M $CaCl_2$

pH of the system was lowest. Any decomposition reaction would be expected to proceed more rapidly when the pH was lower. The idea that Si was responsible for Al "disappearance" seems discredited by this experiment also, provided any mineral which decomposed had a lattice equivalence of Si and Al.

Table 24. Effect of time on pH and Al concentration of the supernatant from 10 g soil in 50 ml. $10^{-4}M$ $AlCl_3$

<u>Time of shaking</u>	<u>pH</u>	<u>Supernatant liquid Al</u>	
		<u>($10^5 \times M$)</u>	<u>% of Max. conc.</u>
30 min.	3.95	3.14	100
7 days	4.52	0.83	26
14 days	4.73	0.56	18
21 days	4.87	0.60	19
28 days	-	0.74	23
35 days	-	0.44	14

In order to get an idea of how the Ca-Al exchange reaction proceeded from its beginning, samples of soil were mixed with $CaCl_2$ solutions and the changes in pH with time noted. Since pH is an indication of Al concentration, the changes in Al concentrations were inferred from the changes of pH. Ten-gram samples of Al-Creedmoor and Norfolk A₂ (Table 5, site 3) soils were mixed with 50 ml. $0.01M$ $CaCl_2$ and the pH's of the stirred suspensions noted periodically. The pH decreased from 5.75 to a minimum of 3.70 in fifteen seconds after addition of the Al-Creedmoor soil, and to 4.38 within fifteen seconds upon addition of the Norfolk A₂

soil. Following this, the pH of the suspension containing the Creedmoor soil increased to 3.89 at two minutes, decreased slowly to 3.76 at twenty-two minutes, but was back to 3.95 after six hours. The pH of the mixture containing the Norfolk soil increased slowly, after the initial drop, to 4.52 after forty-seven minutes. The data are summarized below:

Change in pH upon addition of 10 g Al-Creedmoor
to 50 ml. stirred 0.01M CaCl_2 solution

Time after addition of soil	pH of mixtures	
	Al-Creedmoor	Norfolk A ₂
0	5.75	5.65
15 sec.	3.70	4.38
1 min.	3.89	4.40
2 min.	3.89	4.42
5 min.	3.88	4.45
22 min.	3.76	4.50
47 min.	-	4.52
1.5 hrs.	3.85	-
6.0 hrs.	3.95	-

These results suggest that maximum exchange of Ca for Al occurs when the CaCl_2 solution first comes into contact with the soil. After this there seems to be a slow removal of Al from solution.

Whether soil-solution Al tended to change to solid-phase Al in all acid soil-salt solution mixtures, or if it only happened with some soils, was investigated. This was studied in two experiments; the first, contrasting the Creedmoor and Cecil soils and, the second, using Utah bentonite alone.

Ten-gram samples of the Creedmoor soil (2.46 meq. Al/100 g) and Cecil soil (3.0 meq. Al/100 g) were mixed in polyethylene containers with 50 ml. 0.01M CaCl_2 and placed on a shaker. A container of each soil was taken from the shaker after thirty minutes, 7, 14, 21 and 39 days, centrifuged and the supernatants colorimetrically analyzed for Al.

As before, there was a rapid decrease in solution Al with the Creedmoor, but a slight increase with the Cecil soil (Table 25). These results demonstrate clearly that the "disappearance" of solution-Al from soil-salt solution mixtures is a reaction controlled specifically by the soil material. A plot of these data is shown in Figure 13. Electrolyte adsorption doubtlessly accounts for the lower initial Al concentration with the Cecil soil.

Table 25. Effect of time on pH and Al concentration of the supernatant from 10 g Cecil or Al-Creedmoor soils in 50 ml. 10^{-2}M CaCl_2

Shaking time	Supernatant liquid			
	Al Conc. $10^4 \times \text{M}$		pH	
	Creedmoor	Cecil	Creedmoor	Cecil
30 min.	4.35	2.15	4.01	3.96
7 days	3.65	2.20	4.11	4.02
14 days	2.95	2.22	4.20	4.07
21 days	2.50	2.27	4.21	4.05
39 days	2.10	2.35	4.23	4.00

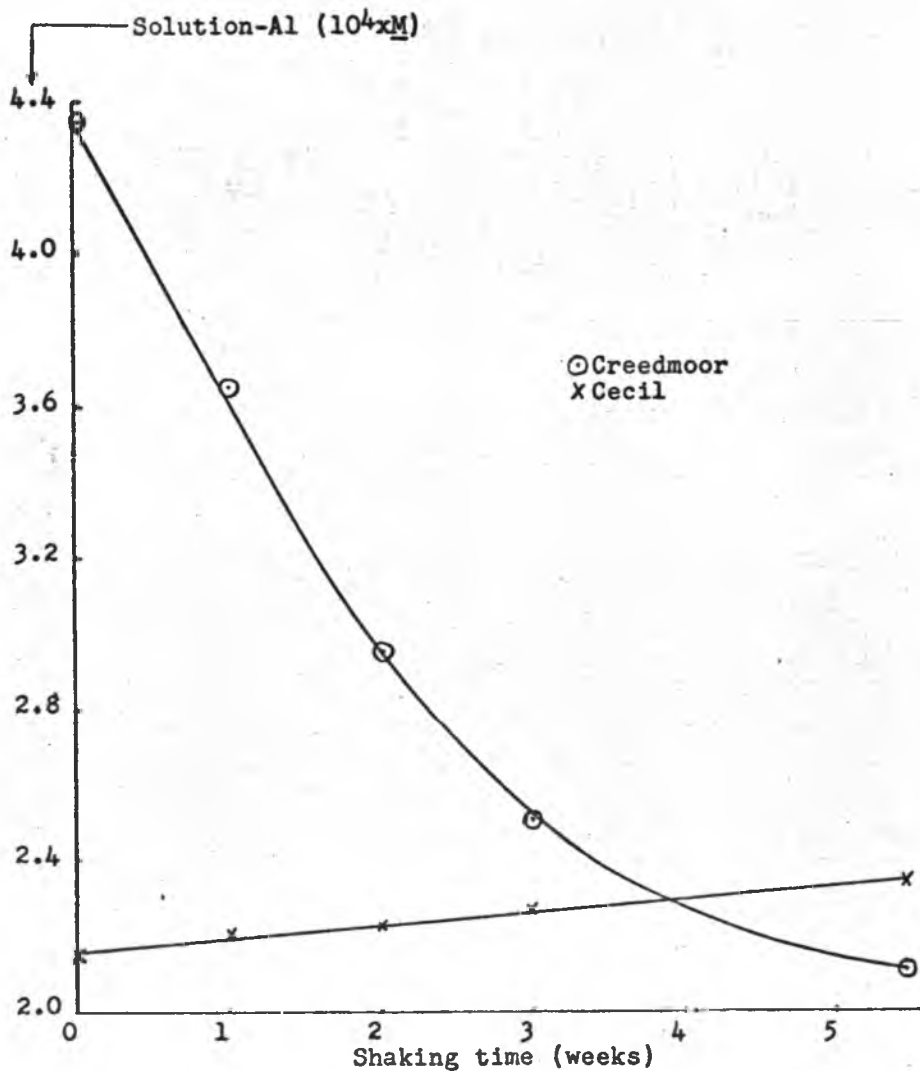


Figure 13. Effect of shaking time on the solution concentration of Al in 0.01M CaCl_2 -Cecil or Creedmoor soils mixtures

The experiment with the Utah bentonite clay was performed a bit differently from previous ones. The samples were shaken in a 70°C water bath rather than at room temperature and because of the high CECp (0.84 meq./g) of the material, only 1 g samples were used. The higher temperature was employed to speed up reactions and thus shorten the shaking times. The samples of bentonite were added to 10 ml. 0.04M CaCl₂, were shaken from thirty minutes to eight days, and the Al concentrations in the supernatant liquids measured (titration with NaOH). The Al concentration seemed to increase slightly during the first two days of shaking, but in general remained unchanged over the eight-day shaking period (Table 26), as was the case with the Cecil soil.

Table 26. Effect of shaking time at 70°C on the concentration of Al in the supernatant liquid from 1 g Al-Utah bentonite clay in 10 ml. 0.08N CaCl₂

Shaking time	Al conc. in supernatant liquid (10 ³ xM)
30 min.	7.65
1 day	8.21
2 days	8.36
3 days	7.92
4 days	7.92
6 days	7.92
8 days	7.92

These two experiments show that the type of soil material is the factor controlling the fate of solution-Al

in soil-salt solution mixtures. The clay mineralogy of the three materials differs widely, but offers no explanation to account for the different results. Montmorillonite-like and interstratified three-layer silicates predominate in the Creedmoor clay. Sizeable quantities of amorphous material are also present. The predominant clay mineral in the Cecil clay is kaolinite, with appreciable quantities of vermiculite. The mineralogy of Utah bentonite differs from other bentonites in that it is well-aggregated. The aggregates are held together by a finely-divided cementing material.

Because the Creedmoor contains appreciable quantities of an interstratified material, probably Al-chlorite, it could be imagined that the soil solution and exchangeable Al, which "disappears", goes to form more Al-chlorite. Such an explanation would have some merit except that interlayer Al is thought to be coordinated with OH-ions (hydroxy-Al). Formation of hydroxy-Al would require the pH of the system to decrease as Al "disappeared" instead of increasing as is the case. For the formation of interlayer Al to account for the loss of solution-Al, the Al would have to be held in an unhydrolyzed, non-exchangeable form. If such a reaction could occur with the Creedmoor soil is not known. Bassett (1958) found that soil vermiculites from Northern Rhodesia contained non-exchangeable interlayer Cu-ions, which were hydrated with H_2O instead of OH. He also demonstrated that

the interlayer Mg (hydrated with H_2O) in a North Carolina vermiculite was very slowly exchanged by K.

Of the mechanisms considered, the release of basic ions from dissolving soil minerals seems most tenable. The mineralogy of this particular Creedmoor soil is not known sufficiently to prove or disprove the hypothesis.

Effects of wetting and drying. The surprising discovery that soil-solution and exchangeable Al "disappear" with time from stoppered soil-salt solution mixtures, suggested a study of the effect of wetting and drying on such "losses" with time. One-gram samples of Utah bentonite (CECp = 0.84 meq. per g) were mixed with 10 ml. 0.08N $CaCl_2$ and were shaken in a 70°C water bath for thirty minutes to eight days. Half of the samples were sealed to prevent evaporation and the others allowed to dry and were re-wet twice daily. Samples were periodically removed from the shaker (the dried samples being made to 10 ml. with H_2O), centrifuged and the supernatants analyzed for Cl ($AgNO_3$ titration) and Al (NaOH titration). The clay samples were analyzed for exchangeable cations by leaching with 1N KCl and measuring the Ca (EDTA titration) and Al (NaOH titration) in the leachates.

The concentration of Al remained essentially constant in supernatants from continuously wet samples, but decreased by 90 per cent from alternately wet and dried samples. The concentrations of Cl in the supernatants followed the

same pattern as the Al concentrations (Table 27).

Table 27. Effect of alternate wetting and drying at 70°C on the concentration of Al and Cl in the supernatant liquids from 1 g samples of Al-Utah bentonite in 10 ml. 0.08N CaCl₂. All quantities of ions are expressed as meq./10 ml.

Shaking time	Conc. of ions in supernatant liquid			
	Al		Cl ^a	
	Wet	Wet & dried	Wet	Wet & dried
30 min.	0.230	-	0.84	-
1 day	0.246	0.213	0.84	0.79
2 days	0.250	0.094	-	0.60
3 days	0.235	0.108	-	0.63
4 days	0.236	0.039	-	0.44
6 days	0.229	0.025	-	0.28
8 days	0.235	0.020	0.80	0.37

^a10 ml. CaCl₂ solution contained 0.824 meq. Cl.

The proportions of Al and Ca countering the CECp of continuously wet samples remained constant, but changed in favor of Ca-saturation with the alternately wet and dried samples (Table 28). The sum of exchangeable Al and Ca seemed to decrease slightly for the alternately wet and dried samples, indicating, perhaps, some blocking of exchange sites by hydrolyzed Al-ions.

To follow up the observation that both exchangeable Al and solution-phase Cl "disappeared" when Al-clay was dried with CaCl₂, a number of small experiments, designed to find the extent to which the reaction would go and to elucidate the mechanism, were performed.

First, one-gram samples of Al-Utah bentonite (CECp = 0.84 meq. per g) were mixed with 2.0 meq. of CaCl₂ and

carried through twelve wetting (deionized water) and drying cycles in an 80°C oven. The samples were not shaken as in

Table 28. Effect of alternate wetting and drying at 70°C on the exchangeable Al and Ca on 1 g samples of Al-Utah bentonite in 10 ml. 0.08N CaCl₂. All quantities of ions are expressed as meq. per sample (1g)

Shaking Time	Exchangeable cations					
	Al		Ca		Sum Al+Ca	
	Wet	Wet & dried	Wet	Wet & dried	Wet	Wet & dried
30 min.	0.598	-	0.216	-	0.814	-
1 day	0.588	0.588	0.219	0.218	0.807	0.806
2 days	0.609	0.515	0.224	0.295	0.833	0.810
3 days	0.592	0.525	0.228	0.278	0.820	0.803
4 days	0.590	0.401	0.228	0.400	0.818	0.801
6 days	0.600	0.370	0.232	-	0.832	-
8 days	0.584	0.319	0.226	0.460	0.810	0.779

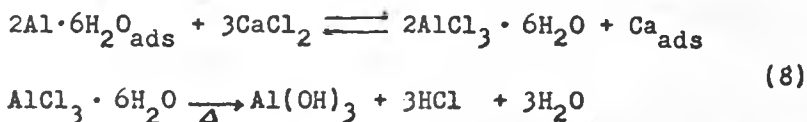
previous experiments. After the twelfth drying, the clay was transferred to a porous crucible, washed thoroughly with water, and leached with a 1N KNO₃ solution. Both the wash water and the leachate were analyzed for Cl (AgNO₃ titration), Ca (EDTA titration) and Al.

The wetting and drying at 80°C resulted in almost complete Ca-saturation of CECp. Of the 2.0 meq. of Ca added, 1.15 was in the wash water and 0.81 was displaced by KNO₃. No Al was detected in the wash water; only 0.02 meq. was in the KNO₃-leachate from one-gram of clay. The wash water contained 1.20 meq. of Cl; 0.80 meq. had "disappeared". The data are summarized below:

One-gram samples of Al-Utah bentonite, CECp = 0.84 meq. per g + 2.0 meq. CaCl₂ carried through 12 wetting and drying cycles at 80°C

	<u>meq. Al</u>	<u>meq. Ca</u>	<u>meq. Cl</u>
Original	0.84	2.00	2.00
Wash water	0	1.15	1.20
KNO ₃ leachate	0.02	0.81	0
Recovered	0.02	1.96	1.20
"Lost"	0.82	0.04	0.80

It would seem that Al displaced from exchange sites by Ca hydrolyzed during drying, or that AlCl₃·6H₂O decomposed to yield an insoluble aluminum oxide or hydroxide, HCl and water, with HCl being volatilized. A reaction sequence of the sort:



would account for the observations.

Although every inorganic chemistry book states that AlCl₃ · 6H₂O decomposes upon heating, to yield "aluminum oxide", HCl and H₂O, the author knows of no work which would show whether or not the reaction would proceed under the conditions which prevailed in the experiments with Al-clay and CaCl₂. Consequently, two 1-meq. aliquots of an AlCl₃ solution were put into pyrex beakers and placed in an oven heated to 80°C. One sample was dried and baked for thirty-three days. The other was wet with deionized water once or twice each day, except for weekends, during its thirty- three

day stay in the oven. After thirty-three days, the samples were removed from the oven and water added to the beakers. There was much white insoluble material in each beaker. The solids were washed by centrifuging, and the wash water analyzed for Al and Cl, with the results shown below:

Sample treatment	Al (meq.)			Cl (meq.)		
	Added	Found	"Lost"	Added	Found	"Lost"
Dried	1.09	0.103	0.99	1.09	0.105	0.98
Wet & dried	1.09	0.120	0.97	1.09	0.125	0.96

It seems clear that $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ indeed does decompose at relatively low temperatures, and that the reaction (8) would be expected to proceed at a fairly rapid rate at 80°C .

Although the insoluble residue material was not completely analyzed, it was found to be soluble in warm dilute HCl, 3 meq. HCl being consumed for each mmole Al dissolved. Specimens of the solid material also were dried, powdered and were subjected to X-ray diffraction analysis, using unoriented specimens. No lines corresponding to any known aluminum oxides or hydroxides were present. In fact, the diffraction patterns were featureless except for diffuse bands at angles corresponding to $d = 9.8$ to 14 angstroms.

Next, a somewhat larger experiment was conducted to find out if reaction (8) would proceed with adsorbents other than Al-Utah bentonite, to see if wetting-drying cycles were necessary, and to establish something about the reaction rate. To this end, one-gram samples of Al-Utah bentonite,

2-g samples of Al-White Store B₂, and 5-g samples of Al-Cecil B₂ were mixed with amounts of CaCl₂ solution as shown in Table 29, and were placed in an oven at 80°C. One-half of the samples were wet with distilled water twice a day; the others were baked continuously. Samples were removed after remaining in the oven, three, seven or thirty days and were analyzed for water-soluble Al, Cl and Ca and for exchangeable Ca and Al.

Except for the Cecil, substantial losses of Cl and of water-soluble or exchangeable Al occurred within three days (Table 29). Almost complete conversion of exchangeable Al to the oxide or hydroxide form, with concomitant loss of Cl and shift to Ca-saturation, had been achieved at the end of thirty days. With the Cecil soil, however, Cl losses were small, and the same quantities of exchangeable Al and Ca were found at all sampling times. The red soil (Cecil), perhaps because of its electrolyte-uptake characteristics, did not respond to desiccation and heat as did the montmorillonite and the soil containing largely three-layer clay.

With the bentonite and the White Store soil, dry storage at 80°C gave the same results, as did alternate wetting and drying at that temperature. This was surprising, since it indicates that ion exchange and hydrolysis reactions can proceed in relatively dry clays or soils. The water contents during baking at 80°C are not known, but must have

Table 29. Reaction of Al-saturated clay or soils with CaCl_2 in mixtures stored at 80°C , either continuously dry, or wet-and-dried twice each day. All quantities of ions are expressed as meq. per sample

<u>Time, days and storage condition</u>	<u>Al in water-wash</u>	<u>Al in KCl-leach</u>	<u>Al Total</u>	<u>Al Lost</u>	<u>Cl in water-wash</u>	<u>Cl Lost</u>	<u>Cl in KCl-leach</u>	<u>Ca+Al in KCl-leach</u>
1 g Al-Utah bentonite								
0	-	0.69	0.69	-	1.04 ^a	-	-	0.69
3 dry	0.02	0.20	0.22	0.47	0.54	0.50	0.48	0.68
3 wet-dry	0.02	0.23	0.25	0.44	0.52	0.52	0.53	0.76
7 dry	0.01	0.13	0.14	0.55	0.44	0.60	0.56	0.69
7 wet-dry	0.01	0.16	0.17	0.52	0.43	0.61	0.58	0.74
30 wet-dry	0	0.04	0.04	0.65	0.37	0.67	0.68	0.72
2 g Al-White Store B ₂								
0	-	0.44	0.44	-	1.04 ^a	-	-	0.44
3 dry	0.04	0.16	0.20	0.24	0.79	0.25	0.24	0.40
3 wet-dry	0.03	0.16	0.19	0.25	0.77	0.27	0.26	0.42
7 dry	0.02	0.10	0.12	0.32	0.69	0.35	0.32	0.42
7 wet-dry	0.02	0.11	0.13	0.31	0.70	0.34	0.31	0.42
30 wet-dry	0	0.06	0.06	0.38	0.64	0.40	0.37	0.43
5 g Al-Cecil B ₂								
0	-	0.12	0.12	-	0.52 ^a	-	-	-
3 dry	0.04	0.08	0.12	-	0.42	0.10	0.10	0.18
3 wet-dry	0.05	0.08	0.13	-	0.45	0.07	0.09	0.17
7 dry	0.05	0.08	0.13	-	0.44	0.08	0.08	0.16
7 wet-dry	0.04	0.08	0.12	-	0.40	0.12	0.09	0.17
30 wet-dry	0.04	0.08	0.12	-	0.42	0.10	0.09	0.17

^aQuantities of CaCl_2 added per sample

corresponded more closely to amounts required for ion hydration than to monolayer coverage (Hendricks, et al., 1940). It is hard to conceive that molecules of CaCl_2 , deposited on clay particle surfaces by evaporation of solvent, can react with exchange sites to free Al-ions, which then hydrolyze. Nevertheless, the results require that a reaction of this kind take place.

An additional experiment, quite similar to the one just described, was performed with the same three adsorbents. The White Store sample used was one of native ion saturation, rather than being Al-saturated. The adsorbent- CaCl_2 mixtures were baked without re-wetting for times up to eighteen days, after which they were analyzed as usual for soluble Ca, Al and Cl and for exchangeable Al and Ca. The results (Table 30) were similar to those obtained in the preceding experiment. While the Cecil soil did not change in Al- or Ca-saturation, other than through ion exchange and electrolyte uptake, the exchangeable Al of the bentonite and the White Store gradually was displaced by Ca and made insoluble, with corresponding quantities of Cl being lost.

Other work, the details of which are not appropriate for inclusion here, showed:

1. Nitrate salts react with Al-clays in a way similar to Cl salts, but not so rapidly. Sulfate salts do not lead to the complete displacement and hydrolysis of exchangeable Al.

Table 30. Reaction of Al or partly Al-saturated clay or soils with CaCl_2 in dried mixtures stored at 80°C . All quantities of ions are expressed as meq. per sample.

Time days	Al in water-wash	Al in KCl-leach	Al Total	Al Lost	Cl in water-wash	Cl Lost	Ca in KCl-leach	Ca+Al in KCl-leach
1 g Al-Utah bentonite								
0	-	0.69	0.69	-	2.17 ^a	-	0	0.69
3/4	0.16	0.47	0.63	0.06	2.07	0.10	0.24	0.71
5	0.08	0.29	0.37	0.32	1.82	0.35	0.42	0.71
8	0.04	0.19	0.23	0.46	1.71	0.46	0.52	0.71
18	0.01	0.06	0.07	0.62	1.54	0.63	0.64	0.70
5 g Native White Store B ₂								
0	-	0.72	0.72	-	2.08 ^a	-	0.45	1.17
3/4	0.27	0.40	0.67	0.05	2.01	0.07	0.73	1.13
5	0.11	0.35	0.46	0.26	1.87	0.21	0.80	1.15
8	0.08	0.32	0.40	0.32	1.81	0.27	0.84	1.16
18	0.06	0.22	0.28	0.44	1.68	0.40	0.92	1.14
5 g Acid-washed Cecil B ₂								
0	-	0.12	0.12	-	1.04 ^a	-	0	0.12
3/4	0.06	0.10	0.16	-	1.03	0.01	0.07	0.17
5	0.08	0.08	0.16	-	1.01	0.03	0.10	0.18
8	0.08	0.08	0.16	-	1.01	0.03	0.10	0.18
18	0.08	0.07	0.15	-	1.01	0.03	0.11	0.18

^aQuantities of CaCl_2 added per sample

2. Nitrite salts react with Al-clays to yield aluminum nitrite, which decomposes readily to yield aluminum hydroxide and nitrogen oxides.
3. Exchangeable H of strong-acid adsorbents (cation exchange resins) is displaced completely on drying with chloride, nitrate or nitrite salts, with corresponding volatilization loss of the anions.

Discussion

The observations reported in this section have dealt with reactions which may have many implications in soil chemistry and mineralogy and in the mineral nutrition of plants.

The observation that solution and exchangeable Al "disappeared", with time, from continuously-wet Creedmoor soil-CaCl₂ mixtures suggested a study of other soils in this regard and also suggested a study of the effect of drying and re-wetting on such losses. Of the three adsorbents studied in continuously-wet systems, Creedmoor soil, Cecil soil and Utah bentonite, Al "disappeared" only with the Creedmoor soil. The conclusion was drawn, though not very well substantiated, that Al "disappeared" due to its precipitation induced by basic ions released from dissolving minerals in the Creedmoor soil. When CaCl₂ was added to the soil the H-ions produced from hydrolysis of Al-ions, exchanged into solution, promoted the decomposition of base-releasing minerals.

The effect of drying and re-wetting acid soil-electrolyte mixtures was to cause a rapid "loss" of solution and exchangeable Al, provided the soil was not a strong anion adsorber. Such "losses" are pertinent to this thesis in that they represent a kind of super ion-exchange reaction, in which desiccation removes end products and pushes the reaction much further toward completion than it would go in a water system, at least in relatively short times. Consequently, equilibrium descriptions of ion exchange reactions involving Al, no matter how carefully established, may be worthless in soils exposed to wetting and drying cycles.

Whether the reactions just described occur at temperatures experienced by soil wetting and drying in the field is not known. It is quite possible, however, that the conversion of toxic Al to $\text{Al}(\text{OH})_3$ by this mechanism was responsible for the observation by Blair and Prince (1923) that roasting a very acid Sassafras soil increased plant growth many-fold. The mechanism responsible for Rich and Obenshain's (1955) observation that drying Nason C-horizon material with AlCl_3 produced a mineral which would not collapse upon K-saturation may have been HCl-volatilization which produced interlayer hydroxy-Al or $\text{Al}(\text{OH})_3$.

SUMMARY AND CONCLUSIONS

A number of plant growth experiments showed that the growth of corn, snap beans, barley and grain sorghum roots into a wide variety of acid subsoils was severely restricted unless lime was added. Where investigated, treatments of the soil with nitrogen, phosphorus and potassium, high phosphate rates or gypsum were ineffective in overcoming the injury. By studying the correlation of root growth to exchangeable and soil-solution aluminum and calcium plus magnesium, it was concluded that aluminum in the soil solution was responsible for the observed injury. The source of this was found to be aluminum countering part, or in some cases practically all, of the permanent charge cation exchange capacity of the subsoil materials.

In the absence of added lime, root growth was invariably found to be least where the quantity of added salt was greatest. The reason for this was the higher solution concentration of aluminum where more salt had been added to the soil. The cations of the added electrolyte increased, by cation exchange, the quantity of aluminum in solution.

Because of the direct dependence of aluminum concentrations in the soil solution on the electrolyte concentration of the system, the idea of a critical percentage of aluminum-saturation which causes aluminum toxicity is minimized. There were indications, however, that, with the addition of "average"

quantities of fertilizer, aluminum injury to roots may be expected when greater than twenty per cent of the permanent charge exchange capacity is aluminum-saturated.

The relation of pH to aluminum concentrations of soil solutions was investigated by equilibrating acid subsoils with salt solutions and measuring the pH and aluminum concentrations in the supernatant liquids. The pH was found to be due largely to the hydrolysis of part of the aluminum-ions in solution. The "practical" hydrolysis constant (pK_h) found to express this relationship varied with the subsoil involved, but generally averaged about 4.6. This differs from the hydrolysis constant for aluminum chloride solutions of similar concentrations. Several experiments designed to find the cause of this discrepancy failed to establish it. The conclusion was reached that aluminum undergoes more extensive hydrolysis in solutions containing soil than in pure solutions.

Construction of adsorption isotherms for Utah bentonite and White Store B₂, using the calcium-aluminum ion pair, demonstrated two things: 1) Aluminum is strongly preferred over practically the entire gamut of equivalent fractions; and 2) Exchange constants calculated for different equivalent fractions vary widely. A study of calcium-aluminum exchange with Norfolk Catena soils, using a total ion concentration, C_0 , of 0.001N, was complicated by failure of exchange equilibria to be established where $c/c_0(Al)$ was 0.2. This

solution had a pH of 4.65, which was concluded to be sufficiently high to cause precipitation of aluminum hydroxide.

In following up an earlier observation that solution aluminum "disappears" from soil-salt solution mixtures with time, it was found that such was invariably the result with the Creedmoor soil, but not with a Cecil soil nor Utah bentonite. Exchangeable, as well as soil-solution aluminum "disappeared" with the Creedmoor soil. The explanation offered for these observations was release of basic ions from "weatherables" in the Creedmoor soils. The mineralogy of the soil was not characterized sufficiently to know if this explanation is tenable.

The effect of alternate wetting and drying on solution and exchangeable aluminum in soil-electrolyte mixtures was investigated. The wetting and drying treatment at 80°C resulted in rapid, and almost complete, "loss" of the two forms of aluminum where White Store soil and Utah bentonite were involved, but not with the Cecil soil. An equivalent amount of chloride disappeared where aluminum was "lost". The reactions responsible for the chloride and aluminum "disappearance" were the volatilization of hydrochloric acid from the system and the hydrolysis of aluminum-ions to aluminum hydroxide. Because the Cecil soil adsorbs chloride, hydrochloric acid did not volatilize from mixtures containing this soil, therefore, no aluminum was "lost".

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